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THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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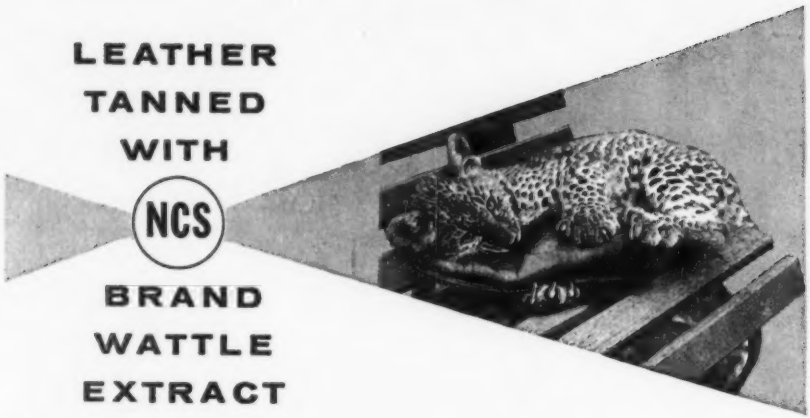

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIV MARCH 1959 No. 3

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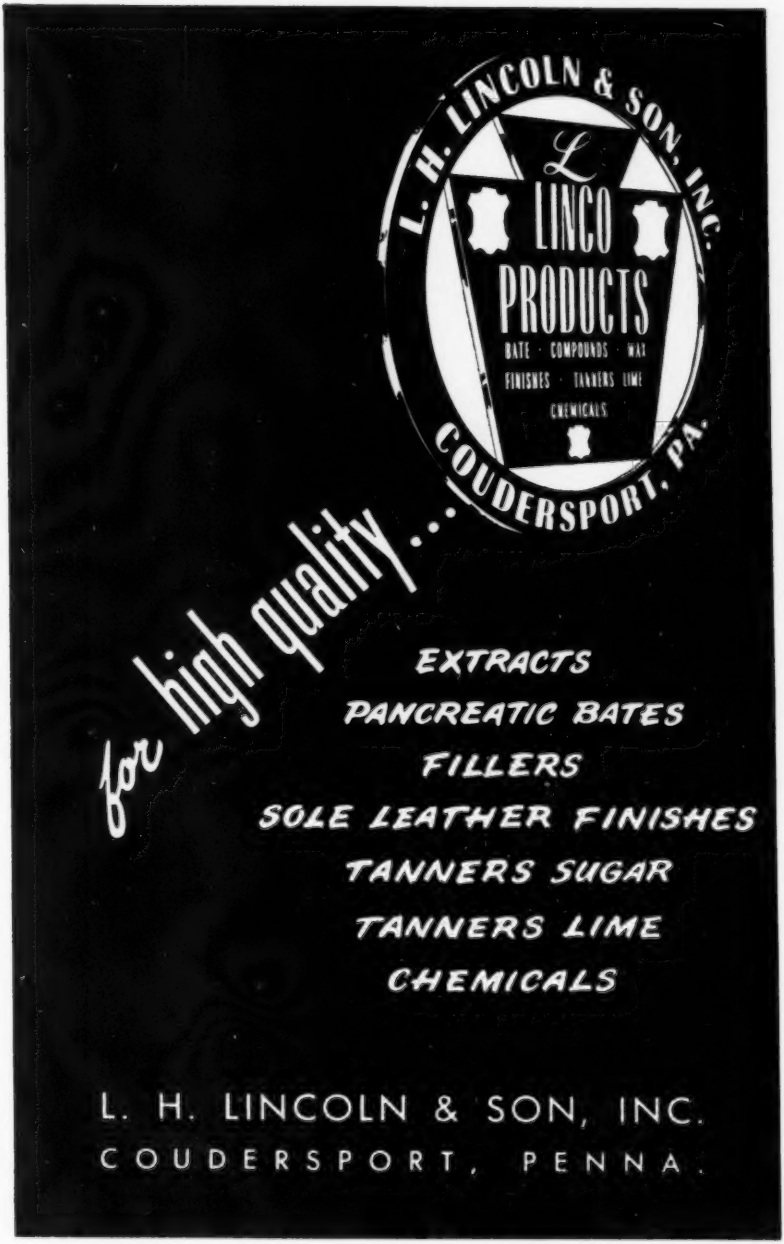
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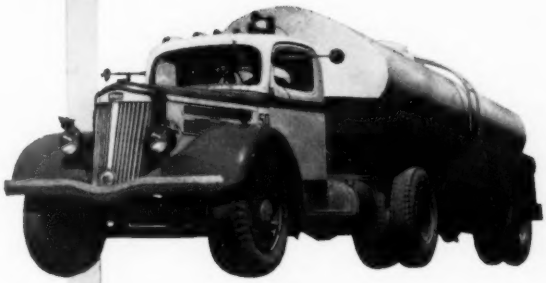

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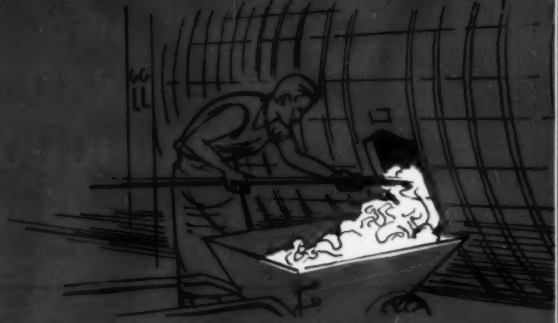

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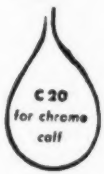

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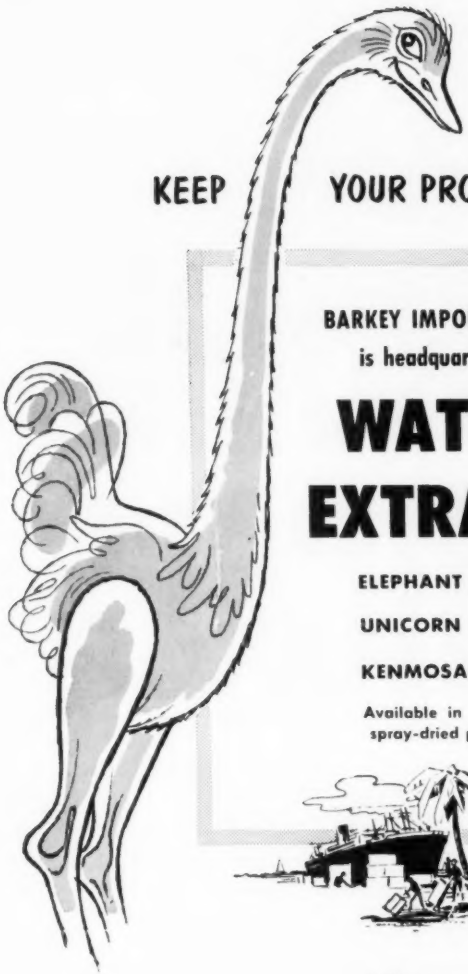

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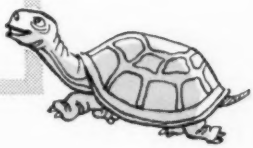

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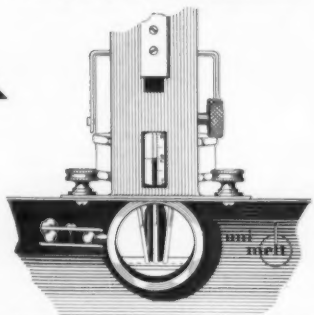

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NOTES FOR CONTRIBUTORS

The following notes are intended to be of assistance to authors submitting papers for publication in this *Journal*. They will be repeated in the January issue each year and should be kept for reference.

General.—It is the objective of the *Journal* to publish papers in all fields pertaining to leather. The papers will normally fall into three broad categories: (1) those which describe basic or fundamental research and make a new contribution to knowledge; (2) those which describe applied research on methods or processes and represent technical progress in leather production, evaluation, or use; and (3) those which review some theoretical or practical aspect of leather chemistry.

Submission of a paper will be held to mean that it will not be published elsewhere unless rejected. It is understood that papers delivered at the annual meeting will be submitted to this *Journal* for consideration and within a reasonable length of time. Papers accepted for publication should not be republished elsewhere in the same form without permission of the *Journal*.

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A PROGRESS REPORT ON THE ENZYME DEPILATION OF CATTLE HIDES*

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ABSTRACT

In a survey of some 40 enzyme preparations for hair-loosening activity, several possessing rather marked activity were found. The relation of depilatory action to hydrolytic activity in these active preparations is shown. The conditions for use of one of the most active preparations are given, and some special equipment devised for studying enzyme activity on hides and skins is described.

Results of tests in which whole hides were treated with enzymes and unhaired on conventional unhairing machines are presented, and the problems encountered are discussed.

—x—x—

INTRODUCTION

The need of the tanning industry for a rapid, economical method of removing the epidermal system from animal hides in preparation for tanning and at the same time alleviating the problem of the disposal of used lime-sulfide liquors from the present unhairing systems is becoming increasingly acute. In a continuation of our previous studies (1) a survey was made of some commercially available enzymes for their depilatory action on steer-hide. The relation of depilation to proteolytic and amylolytic activity is reported elsewhere (2, 3).

MATERIALS AND METHODS

Hides.—The hides used were all from commercial sources. The data given in Tables I and II were obtained from Delph** hides which were obtained from a local tanner. These hides were demanured, fleshed and brine-cured commercially, then stored at the laboratory in moisture-proof bags at

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†Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

**The mention of trade names or companies throughout this paper does not constitute an endorsement by the Department of Agriculture over other products of a similar nature not mentioned.

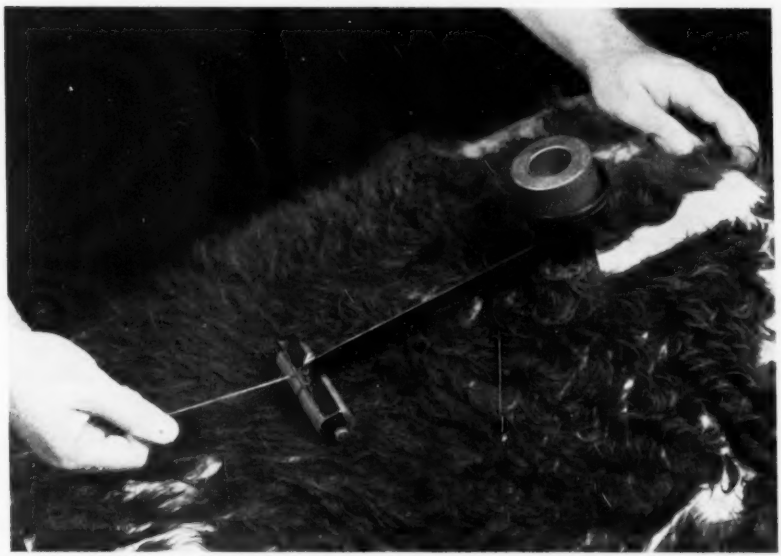
4°–6°F. until needed. Six-inch strips were cut parallel to each side of the backbone in the bend area and two- to three-inch squares were used. They were soaked overnight in a disinfectant solution just prior to treatment. The disinfectant used in the soak water was a 0.03%-solution of BSM-11, a commercial disinfectant, which contains 10% phenylmercuric acetate and 50% potassium 2,4,6-trichlorophenol in undisclosed solvents.

For the data in Table III pieces cut from a commercial green-salted steerhide and calfskin were soaked overnight in a disinfectant solution before use. The goatskin was soaked in a tannery and kept frozen until needed.

The hide pieces used to obtain the data in Tables IV, V, and VI were taken from green-salted hides which had been hand-fleshed, soaked overnight in a disinfectant solution, and kept frozen until needed.

In the full-hide tests green-salted hides were washed in a drum for 10 to 20 minutes, fleshed on a machine, resalted, and stored in moisture-proof bags at about 4°–6°F. until needed.

Estimation of hair loosening.—Hair looseness was estimated by feel and rated from 0 to 5+. For more accurate work the device shown in Fig. 1 was used. The blade, under a constant weight, was pulled repeatedly

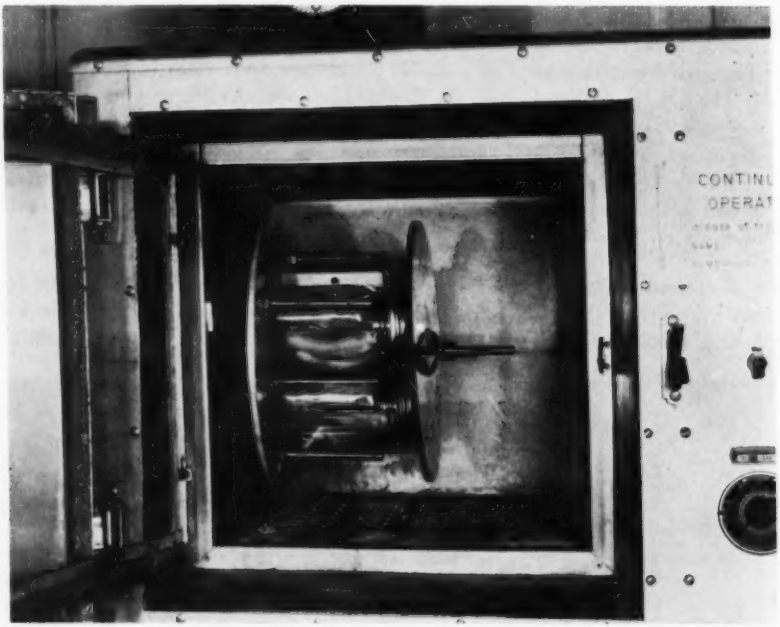


U.S.D.A. Photo by M. C. Audsley

FIGURE 1.—Device for testing the degree of hair loosening of enzyme-treated hides. The instrument measures 9″ in length, has a blade 1″ wide, and exerts 470 grams weight at knife edge.

over the treated hide until no further hair was removed. The number of pulls and the estimated percent of hair removed were recorded.

Special equipment.—Mild agitation has been found to increase the rate of hair loosening. An oven was equipped with a device to rotate small samples of hide in various-sized jars (Fig. 2). An interval timer was used to



U.S.D.A. Photo by M. C. Audsley

FIGURE 2.—Oven equipped with device for rotating hide samples during treatment.

regulate the time the rotor operated. With this device it was possible to control the amount of agitation and the temperature.

In order to determine whether the high proportion of edges on small pieces of hide would influence the rate of unhairing, a device (Fig. 3) was assembled by which the edges were kept out of contact with the unhairing solution. This device consisted of two 4″ funnels with the large-diameter edges ground plane and the stems cut off at a point on the walls so that openings large enough to introduce the solutions would be present. In use the hair was clipped from the edge of 4½″-diameter pieces of hide, and the hide was placed between the funnels, which were held together with aluminum clamps made for assembling glass piping.

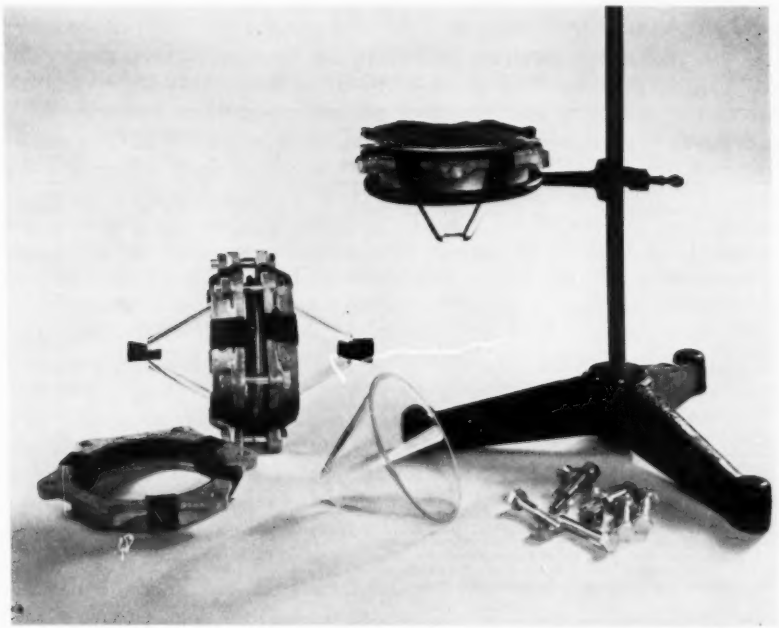


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FIGURE 3.—Device for isolating the hair and flesh surfaces of a hide or skin for independent treatment.

Enzymes used.—From some 40-odd enzymes which were surveyed for depilatory activity (2, 3), the following were included in these tests: HT Concentrate and HT Proteolytic (bacterial enzymes from the Takamine Laboratories), L-56D (a bacterial protease from the Pabst Laboratories), Protease 15 Concentrate (a bacterial enzyme from Rohm & Haas Company), 4511-3 (a bacterial enzyme from the Wallerstein Company), Papain and Bromelin (plant enzymes), and trypsin and pancreatin from the pancreas. These enzymes are described more fully in Table I.

Enzyme assays.—Protease (PV) activity was measured using an adaptation of the Gross-Fuld method (6). The method is based on the principle that the degree of digestion of a casein solution by a proteolytic enzyme, conducted under standard conditions, is proportional to the activity of the enzyme. The digested casein solution, upon acidification, produces a turbidity which is inversely proportional to the degree of digestion. This turbidity is measured with ease and reliability in a photoelectric colorimeter. One PV unit is defined as the quantity of enzyme which digests 1 mg. of casein to

TABLE I

RELATION OF HAIR LOOSENING TO OTHER ACTIVITIES OF SOME SELECTED ENZYME PREPARATIONS

Enzyme	PV(a) Units/g.	Formol Titration(b) meq.-N/g.	DV(c) Units/g.	Concentration Used g./100 ml.	Hair Looseness P(d) R(e)
HT Concentrate(f)	190,000	46.0	95,000	0.1	7–84
HT Proteolytic(f)	331,000	41.8	9,200	0.06	7–83
L-56D(g)	100,000	35.5	4,500	0.19	7–84
Protease 15 Concentrate(h)	162,000	26.7	2,200	0.12	8–77
4511-3(i)	46,300	19.1	17,000	0.41	9–76
Papain	24,800	10.0	<300	0.77	3–97
Bromelin	46,200	46.3	<400	0.41	4–91
Pancreatin 3X USP	66,800	36.6	16,300	0.28	10–25
Trypsin 4X USP Pancreatin	66,500	38.6	3,200	0.29	10–0

(a) Action on casein.
(b) Action on gelatin.
(c) Starch-dextrinizing power.
(d) Number of pulls with scraper. See Fig. 1.
(e) Estimation of percent of hair removed.
(f) Bacterial enzymes from the Takamine Laboratories.
(g) Bacterial enzyme from Pabst Laboratories.
(h) Bacterial enzyme from Rohm & Haas Company.
(i) Bacterial enzyme from Wallerstein Company.

the "standard turbidity end point" in one hour at 37°C. and pH 7.0. The end point corresponds to 78% transmittance through 7/8" absorption test tubes in the Evelyn photometer at 420 mμ.

The dextrinizing value (DV) of the enzyme preparations was measured photometrically using the Tappi suggested method T 643 sm-54(5). One DV unit represents the enzyme activity equivalent to the dextrinization of 20 mg. of Lintner starch in 30 minutes at 30°C. and pH 6.6.

The formol titration values were obtained by allowing the enzymes to react with gelatin solutions under controlled conditions, adding formaldehyde, and titrating with standard sodium hydroxide.

LABORATORY RESULTS

The 40-odd enzyme preparations which were surveyed (2, 3) showed a wide divergence of hair-loosening action. Results with some of the more effective preparations are reported here. Pieces of hide 3" square prepared as described under Materials and Methods were completely submerged in enzyme solutions whose concentrations were chosen to give 19,000 PV units per 100 ml. of solution. The temperature was maintained at 40°C., and incubation was carried out for 17 hours. With the exception of papain the pH values were between 6.2 and 6.5. In order to activate the papain, 0.1*M* $Na_2S_2O_5$ was

used, and the pH of this solution was 5.4. The sulfite in the papain solution also served as a disinfectant. All the other solutions contained 0.015% phenyl mercuric acetate as a disinfectant.

Table I shows the relative unhairing activity of nine enzyme preparations and its relation to some other activities of the preparations. The hair-looseness values are averages of 12 determinations. The concentration of the enzymes was adjusted to give the same PV activity as a 0.1% HT Concentrate which was used as a reference. Thus, if the PV activity were also a measure of hair-loosening activities, then the results obtained should have been the same for all cases. This is obviously not the case. Also the formol titration values, which reflect a type of proteolytic activity on gelatin, are not proportional to the casein digestion values nor do they show any relation to the degree of hair loosening. It is apparent, then, that neither of these assays measures the hair-loosening activity of the enzyme preparations.

The comparatively high hair-loosening value for papain may be partly explained by the large amount used. It is quite possible that the PV activity as determined by the Gross-Fuld procedure does not represent the true activity for papain. It was observed that the natural acidity of the papain lowered the pH of the solution to the point where the casein was precipitated, probably resulting in lowered readings.

There is no apparent correlation between hair loosening and the starch-dextrinizing values (DV) of the enzymes.

On the basis of the hair-loosening results given in Table I the amount of each enzyme required to give equivalent hair loosening was estimated. The values are shown in Table II. Experimental conditions were the same as those given for Table I. For the most part fairly good agreement was obtained. It is believed that these results could serve as a guide for the use of these enzyme preparations in large-scale tests.

Enzyme penetration.—The question has often been raised as to the direction of penetration of the enzyme into the hide and whether much of the activity might not be through the edges when small pieces of hide are used. The device shown in Fig. 3 was used to help resolve these questions. It was found that hide pieces unhaired equally well whether the edges were exposed to the solution or not.

Table III shows the results of penetration studies using 0.1% and 1.0% solutions of HT Concentrate in contact with the hair or flesh side of the hide or skin and rotated in the oven at 40°C. for 17 hours. Under these conditions both concentrations of enzyme loosened the hair from the hide and skins when applied to the hair side. There were differences when the enzyme was applied to the flesh side, and they probably reflect the effect of skin thickness. Neither concentration of enzyme loosened the hair from the steerhide when applied to the flesh side. A 0.1% solution did not penetrate

TABLE II

CONCENTRATION REQUIREMENTS FOR EQUIVALENT HAIR LOOSENING BY SOME SELECTED ENZYMES

Enzyme	Amount Enzyme Used g./100 ml.	Hair Looseness Experiment No. 1 P* R†	2 P R	3 P R	Average P R
Papain	1.0	4–98	2–98	3–98	3–98
Bromelin	0.7	3–97	3–97	2–99	3–98
HT Proteolytic	0.15	3–95	3–97	3–99	3–97
HT Concentrate	0.25	3–98	3–99	3–97	3–98
L-56 D	0.40	5–95	3–97	2–98	3–97
Protease 15 Concentrate	0.70	3–98	2–98	4–96	3–97
4511-3	1.50	5–96	3–98	3–98	4–97
Pancreatin 3 X USP	2.00	3–99	3–94	3–96	3–96
Trypsin 4 X USP	2.00	3–97	3–98	3–95	3–97
Pancreatin					

*Number of pulls with scraper. See Fig. 1.
†Estimation of percent of hair removed.

TABLE III

HAIR LOOSENING BY PENETRATION OF ENZYME FROM HAIR VERSUS FLESH SIDE OF HIDES AND SKINS

Kind of Skin	Enzyme* In Contact With	Concentration % Solution	Hair Loosening
Steer	Hair	0.1	moderate
		1.0	strong
	Flesh	0.1	none
		1.0	none
Calf	Hair	0.1	moderate
		1.0	strong
	Flesh	0.1	none
		1.0	moderate
Goat	Hair	0.1	moderate
		1.0	strong
	Flesh	0.1	moderate
		1.0	strong

*HT Concentrate

calfskin from the flesh side, but a 1.0% solution did. Both concentrations loosened the hair on goatskin from the flesh side.

Since the enzyme is not required to be in contact with the flesh side of the hide to effect hair loosening, experiments were run in which the hair side was simply dipped in or sprayed with the enzyme solution. Pieces of salt-cured hide which had been soaked overnight in a disinfectant solution were run through a clothes wringer to remove excess water. Weights taken before and after dipping the hair side showed the pickup to be about 8% to 10% of the hide weight. The amount of pickup depends on factors such as the residual moisture and the amount of hair. Some other hides tested have held about 15% of solution.

The treated hide pieces were stored in a humid atmosphere and at controlled temperatures. Because of the difficulty of measuring accurately the degree of hair loosening and the variation of individual hides it is not possible to make a hard and fast statement, but usually the hair on salt-cured steerhide dipped in 1% HT Concentrate and held at 45 °C. was loose enough to be easily scraped off in about 3½ to 4 hours.

Conditions affecting hair loosening by HT Concentrate.—One of the enzyme preparations, HT Concentrate, was studied in some detail to learn the best conditions for its use.

TABLE IV

EFFECT OF CONCENTRATION ON DEGREE OF HAIR LOOSENING BY HT CONCENTRATE

	Agitated 40°C., 16 hr.	Not Agitated 45°C. Hours					Not Agitated 25°C., 16 hr.
		1	2	3	4	5½	
Concentration*	Hair Looseness†						
0.075	4+						
0.10	5+						
0.15	5+	0	+	2+	3+	4+	4+
0.25		0	+	2+	3+	4+	5+
0.50		0	3+	4+	4–5+	5+	5+
1.00		0	4+	5+			

*Percent in solution.
†Rated 0 to 5+ where 5+ = hair completely loose.

Concentration.—The results reported in Table IV show that the rate of hair loosening increases as the concentration is increased up to a 1.0% solution. Raising the concentration above 1.0% does not speed up the rate of hair loosening. Experience has shown that the hair on green-salted steer-

hides can be loosened sufficiently for easy unhairing by the action of 0.1% HT Concentrate in 16 to 24 hours at 40°C. with mild, intermittent agitation or in 3 hours by a 1.0% enzyme concentration even without agitation.

pH—The effect of hydrogen ion concentration between pH 3.5 and 9.0, on the unhairing activity of HT Concentrate was studied. Sodium acetate–acetic acid and phosphate buffers were used. Neither buffer system appeared to affect the enzyme activity. Table V shows that the unhairing activity was approximately equal between pH 5.5 and 7.0. Beyond these

TABLE V

EFFECT OF pH ON HAIR-LOOSENING ACTIVITY BY 0.08% HT CONCENTRATE IN ACETIC ACID–SODIUM ACETATE OR PHOSPHATE BUFFERS

pH of Buffer	pH at Finish	Hair Looseness* after 16 hours at 40°C.	Condition of Hide
3.50	3.58	+	plumped, turgid
4.07	4.29	3+	less plumped, much less turgid
4.67	4.90	3+	same as previous
5.10	5.29	4+–5+	firm, not turgid
5.75	6.01	5+	" " "
6.10	6.21	5+	soft, somewhat flaccid
7.00	6.51	5+	soft, flaccid
7.45†	7.11	5+	" "
9.0 †	7.53	3+	not flaccid

*Rated 0 to 5 + where 5 + = hair completely loose.
†Phosphate buffer.

limits it fell off rapidly. The condition of the hide was affected by the pH of the unhairing solutions. Above about pH 6.0 the hide became soft and flaccid, below this point it became increasingly swollen and firm. The swelling of collagen in acid or alkaline solutions is well known (4), and the swelling in this case no doubt reflects the acidity present. However, histological studies have shown that in the higher pH range the elastin was largely destroyed, whereas in the lower range very little attack on this component could be seen. The pH at which the unhairing is carried out might play a significant role in determining the nature of the leather which could be produced from the unhaired hide.

Temperature.—As shown in Table VI, increasing the temperature causes a marked increase in the rate of hair loosening. Temperatures much above 45°C. cause damage to the hide and hence cannot be used.

Hair loosening does take place at 6°C. but at a much reduced rate. After 8 days the hair was completely loose at each concentration shown in Table VI. An interesting phenomenon was observed at this temperature in that

TABLE VI

EFFECT OF TEMPERATURE ON THE RATE OF HAIR LOOSENING WITH HT CONCENTRATE
(*No agitation, 19 hours*)

Enzyme Concentration Percent in Solution	Hair Looseness*				
	Temperature °C.				
	45	30	24	18	6
0.05	4+	3+		+	0
0.10	5+	4+	4+	2+	+?
0.25	5+	5+	4+	4+	+?

*Rated 0 to 5+ where 5+ = hair completely loose.

the entire epidermal layer, including hair follicles and sebaceous glands, was removed intact. This may indicate that at low temperatures a different type of enzyme action takes place.

TESTS WITH FULL HIDES

In view of the promising laboratory results, several tests using full hides were run, and the unhaired hides were tanned into leather of various types. It was found that bacterial growth must be adequately controlled during soaking or severe damage will result when the hide is placed in the enzyme solution and held at a temperature favorable to enzyme action. This temperature is also ideal for bacterial growth. This factor is not so critical when lime is used for unhairing because the high pH of the lime inactivates the bacteria.

Upholstery leather.—In this test six steerhides were soaked 24 hours in water containing BSM-11 disinfectant, 1 part to 1,000 parts hide, then fleshed and placed in a paddle vat in 250 gallons of 0.1% HT Concentrate enzyme based on the weight of the water. Acetic acid and sodium acetate were added to buffer the solution at about pH 5.5. Preservation was effected by using the same disinfectant and concentration as in the soak. The temperature was adjusted and maintained at 38° to 40°C. using live steam. The dilution caused by steam condensation was compensated for by adding calculated amounts of enzyme, buffer salts, and disinfectant. The paddle was run 5 minutes each hour.

This regimen was maintained for about 16 hours at which time most of the hair had come off. However, there was some fine hair still remaining, and in order to further loosen it enough additional enzyme was added to bring the total to 0.15%. The temperature was raised to 43°–45°C., and the paddle was run continuously. After four hours, at which time the hides had been in

the enzyme solution for 21 hours, they were removed and run through an unhairing machine. Unhairing at this tannery was carried out by a sulfide pulping system, and the machine was set for the swollen, turgid hides which that treatment produces. Although it was not possible to change the setting on the machine to accommodate the flaccid hides produced by the enzyme treatment, practically all the hair, including most of the fine hair, was removed.

Three of the hides were bated overnight and three placed directly in the vegetable tanning liquor with the regular stock. The upholstery leather produced was rated satisfactory by the tanner, but some tanners found the grain splits somewhat flat. The flexibles were termed excellent. No difference could be noted in the leather from the bated and unbated hides.

Side upper leather.—These tests were run at the Lowell Technological Institute in cooperation with Dr. Thomas Thorstensen. HT Concentrate was compared at 0.1% and 0.2% concentration in paddle vats using five pairs of sides which had been soaked in disinfectant solution overnight. Difficulty was experienced in maintaining the temperature of the vats, and the hair was not so loose as had been obtained in laboratory tests. There was no noticeable difference between the two treatments. The hair was removed by hand-beaming with medium to firm pressure, although it was thought not to be quite loose enough for unhairing on a commercial unhairing machine.

In another experiment stronger enzyme solution (1%) was sprinkled on the hair side of two sides which were then folded and allowed to stand overnight. The hair on these sides was probably loose enough to be removed on an unhairing machine. All the hides in these tests were unhaired by hand on a beam.

The unhaired hides were rather flaccid, and the grain appeared to be loose. They were placed in a sulfuric acid–sodium chloride pickle overnight, then taken to a tannery, repickled, and made into chrome-retan shoe upper leather. Some tanners found the finished leather satisfactory, others thought it was somewhat flat and firm. Contrary to the condition observed at the time of unhairing, there was no indication of looseness of grain. As a result of these preliminary tests it appears that some modifications will have to be introduced in the tanning process to yield leathers comparable to present commercial production.

Sole leather.—A series of unhairing tests was run with whole hides which were tanned to produce sole leather. Green-salted hides, prepared as described above, were soaked overnight in a disinfectant solution and treated in various ways with solutions of HT Concentrate enzyme.

Several variations of treatment with the enzyme were tested, and although it was possible to loosen the hair to what appeared to be a satisfactory extent,

the standard unhairing machines would not remove all the fine hair. However, in many instances this hair fell out in subsequent processing.

These unhaired hides could be processed through a regular sole leather tanyard after a brief liming (one day); however, most of these were tanned without liming by a modified experimental procedure. Some bends were comparable in physical properties and chemical analysis to conventional sole leather.

DISCUSSION

A number of enzyme preparations have been found which will loosen the hair on animal hides. There may be some qualitative differences in their action on hides, because they show marked differences in activity as measured by various assays. Whether the quality of the leather produced will be dependent upon the specific nature of the enzyme used for unhairing remains to be determined.

Among the problems which need to be solved is that of removal of fine hair. There is evidence that this fine hair may be just as loose as the long hair after enzyme treatment but that because of the soft flaccid nature of the hide, the standard unhairing machines do not remove it. There are several ways this problem might be solved. We have noticed, as have others, that in washing, paddle-bating, etc., the fine hair will come out. Perhaps this is all that is necessary. However, we are now experimenting with other ways of removing the hair. A brush in place of the unhairing blades seems to hold promise.

Another perplexing problem is the inconsistency of results. An unhairing procedure may give excellent results with one trial and poor results at another time without any apparent change in the conditions. This may be due to some undetected factor that is not being controlled or perhaps merely to differences in the raw stock. We hope to find out.

We are well aware that the hides produced by enzyme unhairing differ both chemically and physically from limed hides and that changes in processing will undoubtedly have to be made to produce high-quality leather. Much of our effort will be directed toward this end.

SUMMARY

Nine enzyme preparations, selected for depilatory activity from a recently surveyed group of 40, are compared as to their ability to act upon casein, starch, and gelatin. Their comparative hair-loosening ability is also reported. Some special equipment is described. Results showing the direction of penetration of enzymes into hides and skins are given. The effects of concentration, pH, and temperature on hair loosening by one enzyme preparation are reported.

Some larger-scale tests in which whole hides were treated with enzymes and unhaired on conventional unhairing machines are presented. Some of the problems encountered and possible solutions are discussed.

ACKNOWLEDGMENTS

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REFERENCES

1. Cordon, T. C. *JALCA*, **50**, 270–74 (1955).
2. ———, H. W. Jones, A. L. Everett, and I. D. Clarke. *Bacteriol. Proc.*, **1957**, 26.
3. ———, ———, I. D. Clarke, and J. Naghski. *Appl. Microbiol.*, **6**, 293–97 (1958).
4. McLaughlin, G. D., and E. R. Theis. *The Chemistry of Leather Manufacture*. ACS Monograph No. 101. New York: Reinhold Publishing Corporation, 1945.
5. Tappi Suggested Method T 643 sm-54, Dextrinizing Value of Enzymes (Enzyme Activity), *Tappi*, **37**, 113A (1954).
6. Tauber, H. *The Chemistry and Technology of Enzymes* (New York: John Wiley & Sons, 1949) p. 181.

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DISCUSSION

Dr. Turley (Rohm & Haas Company): To those who work in this field this is a fascinating process and also full of difficulties. I think if the enzyme methods of unhairing had been relatively simple and straightforward, we would have had successful methods for removing the hair by means of enzymes a long time ago and they would possibly be used widely in the industry.

Of course the enzyme methods go back to World War I and originated in Germany, and they did encompass using alkaline swelling agents prior to the enzyme. They had a limited success and more or less died out. And then this whole field was resuscitated again in 1953, by Burton, Reed, and Flint in England.

Due to the changed situation today with regard to tannery effluents the whole subject has become important again. Burton—and probably Dr. Flint, who worked with him—stressed the question of mucopolysaccharides and the use of mucolytic enzymes. Some of them gave positive results, but believe the results were due more to the proteolytic enzymes that the

products contained, since they were commercial products. Since that time Dr. Cordon and his school are finding that the diastatic activity has no relation to the unhairing activity, and I imagine that idea will be dropped.

Further, there is the difficulty in relating unhairing action actually with the proteolytic activity of the enzyme as measured by what we used to call the Fuld-Gross method, but is now referred to here as the Gross-Fuld method. There will probably have to be a breakdown into some other types of proteolytic enzymes.

Dr. Cordon is quite frank to admit that one of the problems is the inconsistency of the results. Perhaps in discussion here somebody might be of help in that direction and shed some light on some of these problems. As far as inconsistency is concerned, I wonder whether Dr. Cordon has had in mind the effect of the autolytic enzymes present. They may be operative under some conditions and depressed under other conditions. I say that because of the interesting results that are obtained at quite low temperatures, given enough time, by using no enzymes at all. Apparently under some conditions the hair will slip very readily. It might be due to residual autolytic enzymes.

Another important point is the question of the quality of the leather. No process using enzymes is going to be successful if good quality leather cannot be made. It is rather interesting to see that the leathers made with the vegetable process were considered satisfactory but that those put through the chrome process were not considered satisfactory. I am going to ask Dr. Cordon if he has anything to say on that.

I would like to say this, just before throwing the meeting open to general discussion: There has been a lot of talk about the new enzyme unhairing processes of today. But I am not aware whether in Europe or in this country there is yet a successful process which will operate under practical conditions, day in and day out, on large quantities of hides. Those problems are still in front of these workers. I want to point that out.

A first question—the question of the autolytic enzymes; and second, the difference between the vegetable leather and chrome leather, if Dr. Cordon will say a few words on it.

DR. CORDON: I have observed that on occasion the hair becomes loose without any enzyme being present. One very striking thing happened. We had a piece of hide that was frozen in a deep-freeze chest. We sampled it periodically over a year and a half and noticed that as samples were taken they became increasingly easy to unhair. Just recently we took a piece out and thawed it and found no enzyme was needed to loosen the hair. You could brush the hair off, epidermis and all. It had been kept frozen at −10°C.

in a deep-freeze chest all this time. So something does go on. I have noticed other cases where the hair has become loose sitting in a disinfectant solution. But this is not consistent, and I would hate to depend on it as an unhairing process. I think it may play a role in causing some of these inconsistencies that we are experiencing.

As to the leather quality, we have produced good vegetable leather. We have not as yet produced satisfactory chrome leather. That is a project we intend to work on. We don't know whether we can do it, but we hope we can. We feel that enzyme unhairing is sufficiently important to justify our spending effort to try and solve this problem.

DR. TURLEY: We hope to see you continue, Dr. Cordon, and solve this problem. I would like to call on one or two men here who have in the past had some experience with the use of enzymes in unhairing. Would Dr. Pfannmuller care to say a few words or ask a few questions?

DR. JULIUS PFANNMULLER (Wallerstein Company): I think Dr. Cordon's report was very encouraging in one way and in another way not. I think the really scientific approach would be to try to work with pure enzymes.

You can take crystallized enzymes, as for instance, crystalline trypsin or bacterial proteinases separated from amylases. You can get practically every enzyme either crystalline or in a concentrated, highly purified form, and such preparations might give you some important leads.

The difference in time of enzymatic hair loosening on thick pieces of hide versus goatskins might depend upon the time required for the enzyme to penetrate to the hair roots. This penetration has to occur especially from the flesh side. Of course, this penetration also depends on how the hide or skin was treated previously, that is, on whether the fiber structure is open and so gives the enzyme a better opportunity to penetrate to the roots.

You mentioned your experience of fine hair left over, which could not be removed properly by a mechanical unhairing machine. We have frequently observed that the fine hair after enzymatic loosening can be removed by drumming, because the hair is often loose. However, the mechanical unhairing rolls cannot grasp the hair.

I think we should also stress the economics of this process. Economic aspect plays a big role for the tanner, especially now. Highly concentrated enzyme preparations cost a lot of money, and while one should use them in laboratory experiments, they are too expensive for commercial use.

I think enzymatic unhairing is cetainly a very fascinating problem, but it is far from being solved yet. That is my personal opinion, of course.

DR. CORDON: I agree one hundred percent. It is not solved. The enzymes are costly. We are trying to get at some of these fundamental problems in different ways—using purified products, using inhibitors, using different assay procedures to see if we can correlate an assay with hair loosening, and we feel that by gaining fundamental information of the mechanism of hair-loosening reaction we may learn just what is needed to remove the hair and do it more economically.

I think the enzyme companies could do a good deal if they would try to produce cheaper products. Many of these enzymes shown here are for food use. However, we do not need highly purified preparations to treat hides.

DR. PFANNMULLER: One more question. You mentioned a hide that you kept in a freezer for a long time. Did you make any microbiological tests about changes which might have occurred, or did you test skin sections microscopically as to what might have happened to the fiber structure?

DR. CORDON: No, we have not done this, but we could. We still have some of the material left.

DR. PFANNMULLER: I would be very much interested to know if the fiber bundles were broken.

DR. TURLEY: Would Dr. Thomas Thorstensen care to enter this discussion? He has done work in this field.

DR. THOMAS THORSTENSEN: I would like first to thank Dr. Cordon for his paper today. Dr. Cordon's work has been very helpful to us in the past, and I hope it will be continued. I agree, however, with Dr. Pfannmuller that the investigation of pure enzymes would be of great practical value in this field.

In the Tanners' Council beamhouse research project we have been working extensively with enzymatic unhairing. We have run numerous tests of various size on kid, calf, and cattle hides in several tanneries. Some of the problems Dr. Cordon mentioned are very real to us; others we feel have been solved.

A year ago, after Dr. Cordon's last paper on enzymatic unhairing, the remark was made, "It seems to be fashionable to work on enzymatic unhairing". In my opinion there is good reason for this to be the case. I think that enzymatic unhairing is much closer to being a commercially practical reality than most people here realize.

DR. TURLEY: Of course I think the big hurdle for all of these things is not the first stage—finding the enzyme to take off the hair—but to put it across and find out how to make good leather on a large scale. That is what demands a lot of work, and service too.

CLARENCE W. BEEBE (Eastern Regional Research Laboratory): I would like to say that I tanned that vegetable sole leather for Dr. Cordon. Dr. Turley asked why it made good vegetable leather but not good chrome leather. To obtain good vegetable leather required some adjustment of the pH to get the results that we did. So it is possible that the chrome leather, if adjusted properly, would also make good leather.

DR. TURLEY: When you adjusted the pH values, can you tell us how high you had to go?

MR. BEEBE: We went to pH 4. You could put it in lime first, if you wish, and then you could treat it just like an ordinary limed hide. But we adjusted to pH 4 and then used the rapid tanning process that has been developed and used in England, and with some success, by adjusting hides to pH 4 and tanning at pH 4.

DR. TURLEY: So it is unnecessary to use alkali?

MR. BEEBE: We did not have to use any alkali at all after we got rid of the calcium salts.

DR. TURLEY: That is very important, indeed.

MR. BEEBE: We were able to tan completely in 48 to 72 hours. We were able to penetrate completely.

DR. TURLEY: With straight vegetable tannins?

MR. BEEBE: Yes.

DR. TURLEY: That is a fine statement, Mr. Beebe.

DR. THEODORE D. BRAUNSCHWEIG (Loewengart and Company): I am interested as to whether the hides which you stored in the freezer have been stored open or packed?

DR. CORDON: Packed in polyethylene bags.

DR. BRAUNSCHWEIG: You know that if you store food in a freezer, it acquires, after a certain time, a special taste which is very much disliked, in the form of "food burn" or "freezer burn." I know that from storing food. I wondered whether the change which took place in your material has any similarity to the change which comes over food when it is stored in a freezer?

DR. CORDON: I don't know. We didn't taste it. [Laughter]

DR. ALBERT BOIDIN (Société Rapidase, Sedin, France): I was wondering about the problem of the inconsistencies. I have a little bit of experience with enzymes, and two possible explanations come to mind. One is the presence of heavy metals as inhibitors or agents toxic to the enzyme. The other is the degree of denaturation of the protein itself, because many of the proteolytic enzymes appear to work much better if the material is partially denatured and then submitted to the enzymes.

DR. CORDON: We have not investigated heavy metals. It is possible that they could be active. I do know this: that you are certainly correct in that denaturation could be a factor. Whether it is a factor in unhairing, I don't know. I do know that if a piece of hide has been denatured even with mild heat or any other mild denaturing agent, this enzyme will attack it readily—that is, it will attack the collagen. Whether there is denaturation in the epidermis that affects this hair loosening, I do not know. These are problems we will look into, and we hope to find the answers.

Boegel's Process of Quick Tanning. The green hides are depilated and soaked in the usual manner. They are then placed in a solution of any vegetable tannin or a solution containing a mixture of several vegetable kinds of tannin. To this are added acetate of alumina, chloride of soda, and picric acid, in alternate smaller or larger quantities, according to the nature of the skins. As an average, 50 pounds of acetate of alumina, 10 pounds of chloride of soda, and a like quantity of picric acid are used to 200 pounds of vegetable tannin. This tanning fluid produces calf leather in 14 days, kip leather in 3 to 4 weeks, bullock leather in 5 to 6 weeks, sole leather in 6 to 8 weeks; the quality of the different kinds of leather being such that they cannot be distinguished from leather tanned in the ordinary manner.
—*The Techno-Chemical Receipt Book.* Philadelphia: Henry Carey Baird & Co., 1903.

SEMIMICRO TECHNIQUES FOR EVALUATION OF LEATHER FINISHES*

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INTRODUCTION

There are many factors which play a role in the formulation of a good leather finish, about which very little has been published. In formulating a basic research program in this area many questions come to mind. Much work has been done in recent years on measuring the adhesion of a finish to a leather surface (1–3). In addition, anyone working with finishes wants to know the factors which affect flow-out characteristics, penetration rate, depth of penetration of the finish, streaking, break, etc.

In studying these problems we have utilized two techniques which are giving us answers to some of these questions. The techniques are simple, cheap, and accurate.

FIRST TECHNIQUE: MICROSCOPY

One method which has been in use at the Rohm & Haas Finish Laboratory for some time is to examine the deposition of a finish by microscopy. The colored pigments in a finish are easy to locate by this means. However, a new development which has aided us considerably is the development by the Tanners' Council Laboratory of a technique suitable for the staining of acrylic polymers. This method was employed by that laboratory for locating acrylic polymers deposited in leather during impregnation processes (4). We have employed this method to study leathers finished with various swabbing and spraying techniques and have acquired some very interesting information.

Procedure.—The procedure adopted for microscopy was as follows: A small piece of the finished leather was cut out of the area to be studied. This piece, approximately ¼" x ¼", was soaked in water until thoroughly wet, mounted in a drop of water on the stage of a freezing microtome, and frozen. Cross sections were then cut to thicknesses varying from 25 to 50 microns, depending on the type of leather. In general it was advisable to cut sections of vegetable-tanned leather thicker than those of chrome leather

*Presented at the Fifty-fourth Annual Meeting, Swampscott, Mass., May 27, 1958.

in order to maintain sufficient coherence of structure during subsequent handling. The cut sections were then washed by immersion in water. When no staining was to be done, the sections were mounted directly onto a microscope slide in glycerin jelly under a cover glass. If the sections were to be stained, they were placed in the phenylhydrazine stain advised by the Tanners' Council Laboratory (4, 5) for 15–30 minutes, then washed with two successive changes of water, and similarly mounted. If white leather is to be studied, it is advisable to stain a control section of the unfinished leather, because in some of these leathers fillers are used which contain starch, and if the starch is partially hydrolyzed, it may also react with the stain.

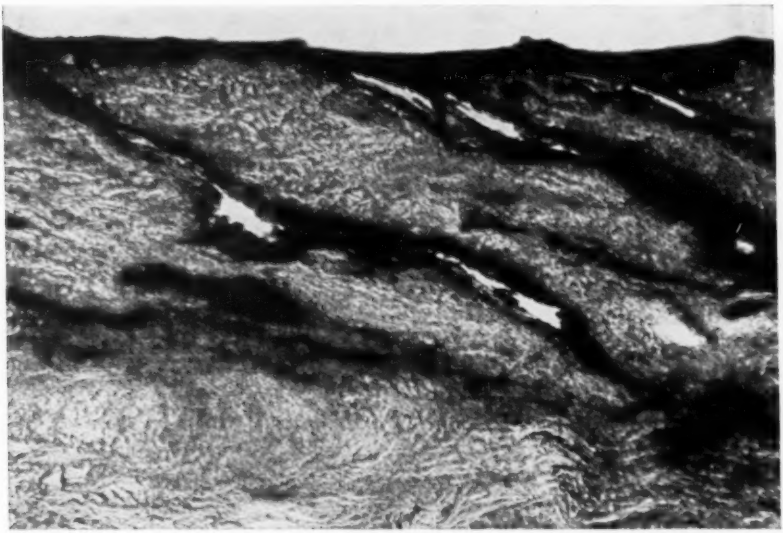

FIGURE 1.—White side leather after the first swab coat, stained to show methacrylate penetration. Photographed by transmitted light at × 125.

Figure 1 shows a stained section of chrome-tanned side leather finished white after application of the first swab coat. This section was photographed by transmitted light. The pigment is opaque and hence shows up dark in the photograph. The stained acrylic polymer can be viewed because of its color, which is yellow, but because a light source rich in blue light was employed, it shows up with a slightly greenish hue in this particular film (Anscochrome). Note that the pigment has been entirely filtered out by the leather surface. Its only penetration is into the hair follicles. The binder, on the

other hand, penetrates through the grain surface. It enters in not only from the surface but also through the periphery of the hair follicles.

FIGURE 2.—White side leather after the first swab coat, photographed by dark-field illumination at × 81.

Figure 2 is a black-and-white print of a similar section viewed by dark-field microscopy. Here the pigment is high-lighted, and the color of the acrylate is minimized, thus showing plainly the pigment deposition.

Figure 3 is a photograph of an unstained section of vegetable-tanned upholstery leather which has been swabbed with a metallized brown base coat finish. The principal thing to note about this photograph is that there is very little or no entry of the hair follicle by the pigment. We have not seen any such entry as yet in this type of leather. At first it was believed that this was due to the fact that our early studies were made only on spray-finished vegetable-tanned leather. However, it seems to be true also of swab-finished upholstery leather.

FIGURE 3.—Metallized brown upholstery leather after the first swab coat, photographed by transmitted light at × 63.

SECOND TECHNIQUE: PENETRATION RATE MEASUREMENTS

In considering the application of an emulsion type of finish formulation to leather, several factors must be considered:

1. The tendency of the formulation to wet the surface of the leather. This will affect flow-out.

2. The viscosity or resistance to flow of the formulation. This will affect flow-out and tendency to streak.

3. The gelation time of the emulsion. This will affect the height of the finish on the leather (coverage) and the nature of the film produced (toughness, continuity, etc.). Brown has presented an excellent discussion of gelation factors in a recent paper (6).

4. The effect of the evaporation rate and the water-absorptive character of the leather surface on the viscosity and the gelation rate.

We have devised an apparatus which provides information on the interplay of these variables and which gives us what is apparently an index of how a formulation will behave on leather. Basically, the technique is as follows: The specimen in question is placed upon a stage and is adjusted so that the area to be used is in a horizontal plane and perpendicular to the focal plane of the camera. A condensed light source back-lights a droplet of formulation on the specimen, creating a shadow-like image which in turn is projected onto the ground-glass screen of the camera. The use of a lens with short focal length at a long lens-to-focal-plane distance creates a magnified image. (The formula for determining magnification is:

$$\text{Magnification} = \left(\frac{\text{lens-to-focal-plane distance}}{\text{focal length of lens}}\right) - 1$$

Our average magnification in this work was 17.3.)

In cases where conditions change quickly, a rapid method of film change must be used. The majority of our work was done with Kodak Tri-X "film packs" whereby 12 successive exposures may be made by simply pulling a paper tab for each cycle. The individual frames are prenumbered, providing a permanent record of the operation.

Apparatus.—The equipment used in this series is shown in Fig. 4 and described below:

The Camera.—A 4″ x 5″ Burke and James View Camera modified by the addition of braces needed to provide maximum rigidity when working at direct magnification was used. It can be noted at this point that in photomacrography, magnification is controlled by movement of the rear standard (film plane) and final critical focus by use of the front rack and pinion mount.

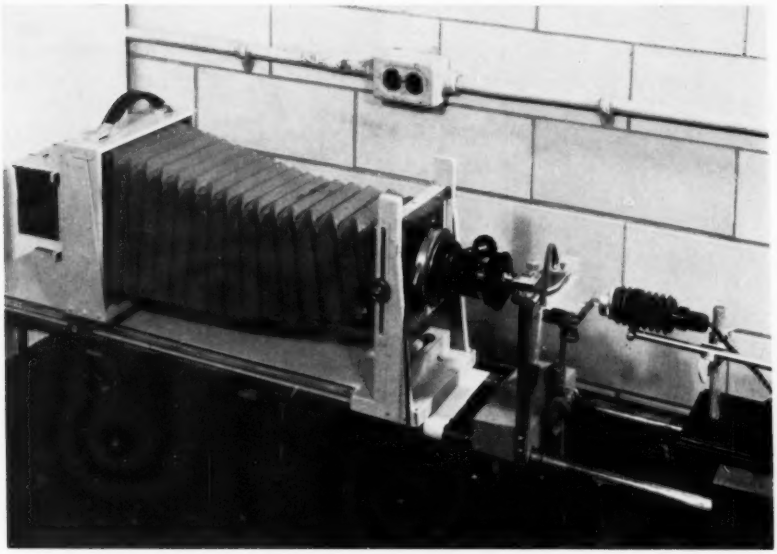

FIGURE 4.—Apparatus for measurement of penetration rate.

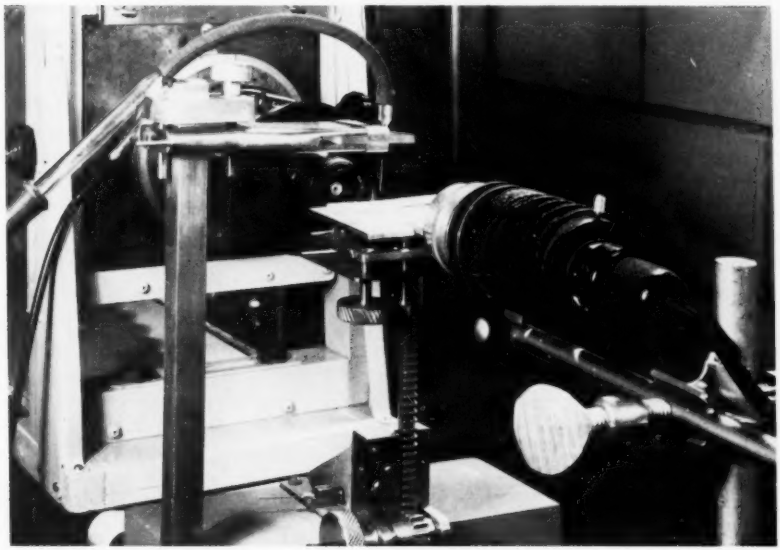

FIGURE 5.—Close-up of stage showing knobs controlling movement.

Lens and focusing mount.—The lens used in our particular series was a 32-mm. focal length Bausch and Lomb Micro Tessar. Since magnification is a function of bellows "draw" or lens-to-focal-plane distance, a short-focus lens is generally necessary. This particular lens is especially designed for photomacrography and produces excellent results. The focusing mount is also available from Bausch and Lomb and allows a high degree of accuracy and ease in focusing.

The specimen stage.—Since any physical clamping might alter fiber orientation of the leather specimens, it was decided simply to lay the specimen in approximate position on the stage. Working at magnification also emphasized surface irregularities and thickness differences. Figure 5 is a detailed illustration of the stage. The stage was designed to provide vertical movement for thickness compensation and movement about both horizontal axes for irregularity compensation. Also illustrated is the "needle holder" used in the accurate placement and adjustment of the solution-dropping needle. Since the needle is located at the center of the droplet, it provides the logical focusing point. It can be noted that the needle-to-specimen distance is determined on the camera focusing panel very accurately by the vertical adjustment of the holder. Because of a screw-thread mechanism the needle holder also allowed ¾ inch lateral movement which simplified the replacement of the needle into the correct position relative to the focal plane after successive fillings and cycles.

Light source.—An American Optical Co. "Spencer Universal" microscope lamp was used. It provides relatively uniform illumination over the entire field at low heat and wattage.

Procedure.—A drop of the material whose penetration rate was to be determined was released from a No. 25 gauge hypodermic needle onto the leather surface. All needles employed had their bevels removed. The drop was released from a set height (3.33 mm.) above the leather surface. As explained above, the magnified image of the drop (Fig. 6) was photographed. This was done as soon as the drop landed and at frequent timed intervals thereafter until gelation occurred or, as in the case of deionized water, complete absorption had taken place. The apparatus was kept in a room conditioned at 70°F. and 65% R.H., and the samples of leather employed were conditioned in this room prior to use. This was to minimize any differences due to varying moisture content of the leathers or evaporational effects.

On occasion it was desired to test the effect of atmospheric variation. In such cases the leather was conditioned over water in a desiccator prior to use, and the measurements were made in a specially constructed Plexiglas chamber shown in Fig. 7. This chamber was constructed to hold small amounts of water in compartments on both sides of the leather sample. The lid is closed

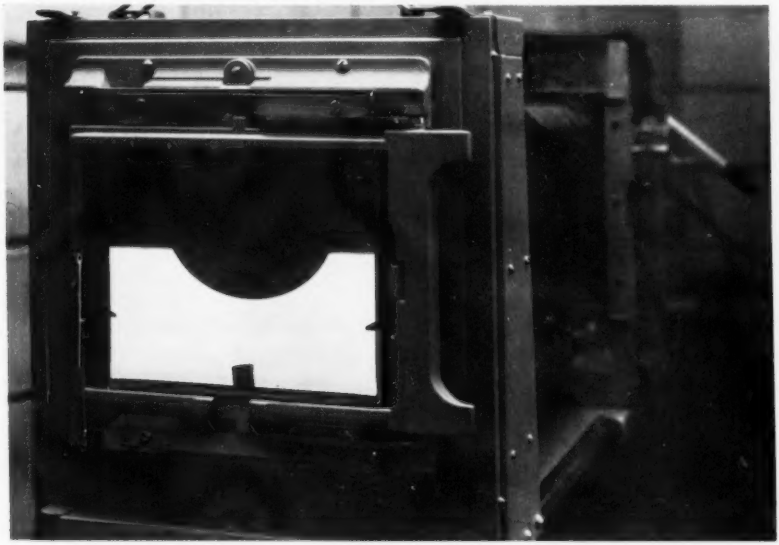

FIGURE 6.—Image of a drop of finish on leather as seen through the view plate of the camera.

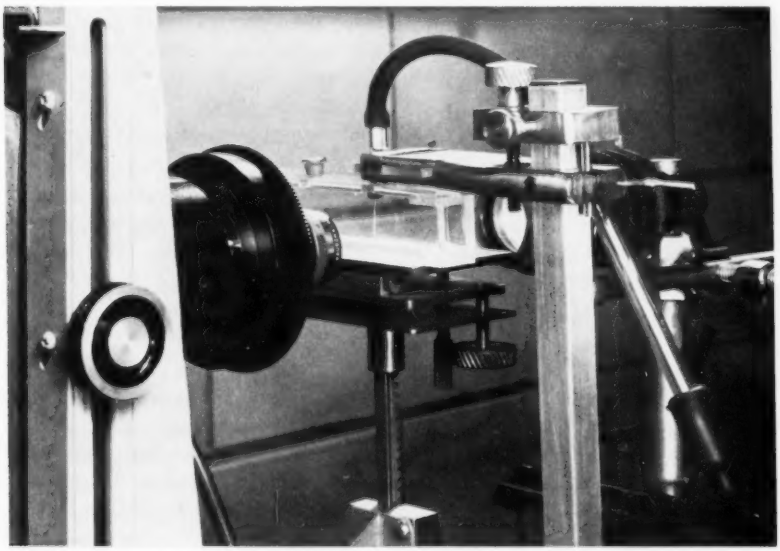

FIGURE 7.—Close-up of stage showing special chamber for work in a saturated atmosphere.

with a Vaseline seal, and the needle is introduced through a small rubber stopper such as that employed to seal ampoules for hypodermic injection.

Measurements of the volumes and/or the contact angles of the drops with the leather surface were made directly from the photographs. Hence, these measurements could be made carefully and at leisure in spite of the fact that we had a rapidly changing system due to absorption by the leather surface. Furthermore we had a permanent record to which we could always refer.

Volume was computed by the equation for the volume of a spherical segment:

$$V = 1/6\ \pi h(3r^2 + h^2)$$

where V = the volume of the drop remaining on the surface,
h = the height of the drop at its highest point, and
r = ½ the width of the base of the drop.

In addition to determining the volume of a drop on the surface we also measured the contact angle of the drop on the leather surface. The contact angle is a measure of the wettability of a surface to a liquid. Glasstone (7) gives a good explanation of the phenomenon. At equilibrium the forces acting at the interfaces must balance, and assuming that these can be represented by surface tensions acting in the directions of the surfaces, it follows that

$$\gamma GS = \gamma LS + \gamma GL \cos \theta$$

where γGS = the interfacial tension between the gas (in this case air) and the solid,
γLS = the interfacial tension between the liquid and the solid,
γGL = the interfacial tension between the gas and the liquid, and
θ = the angle of contact between the liquid and the solid, measured in the liquid.

From this it follows that

$$\cos \theta = \frac{\gamma GS - \gamma LS}{\gamma GL}$$

Therefore, anything which increases the attractive forces between the liquid and the solid, i.e., lowers the interfacial tension between them, increases the value of the cosine of θ, thus making θ, the contact angle, smaller. Similarly, wetting agents, by lowering the tension between the gas-liquid interface, exert a similar effect. Hence the wettability of a surface by a liquid is inversely proportional to the angle of contact, i.e., the lower the angle, the greater the wettability.

The direct measurement of the contact angles on our photographs can easily be obtained by measuring with a vernier the base of the drop and its height and utilizing the equation

$$\tan \frac{\theta}{2} = \frac{2h}{W}$$

where θ = contact angle,
h = height of the drop, and
W = the width of the base of the drop.

Because of the smallness of the drop which we employed, the effect of gravity in flattening the drop was minimized. Employing the correction (8) made a difference of only approximately 1° in most of the contact angles. Therefore, in most of the work described in this report, uncorrected values were employed, particularly since we were more interested in comparative than in true values.

FINDINGS

High contact angle of water on leather.—Fig. 8 shows some photographs from a typical sequence where water was employed on corrected-grain chrome-tanned side leather.

The initially very high contact angle of water on leather confirms the findings referred to by Beakbane (9) and work done at the Tanners' Council Laboratory (10). The British workers attribute this high initial angle of contact to the roughness of the leather surface, which causes a grid-like structure which has an artificially high contact angle. Their reference to the effect of the structural network in a duck's feather on water resistance (*op. cit.*) is a good one and is confirmed by the experiments of Cassie and Baxter (11), who demonstrated that the effective contact angle is determined in part by the dimensions of the fibers making up a grid-like structure and their distances apart.

We have some further confirmation of this to which reference is made in a later section of this report. However, as Beakbane notes, the contact angle of water on dampened leather is considerably lower than that on dry leather. The changes in the character of the collagenous tissue in the leather surface which occur on hydration undoubtedly play a very large role in the change in wettability of the surface. Every tanner knows that dried leather has an initial resistance to wetting, but when this initial resistance is once overcome, it wets rapidly.

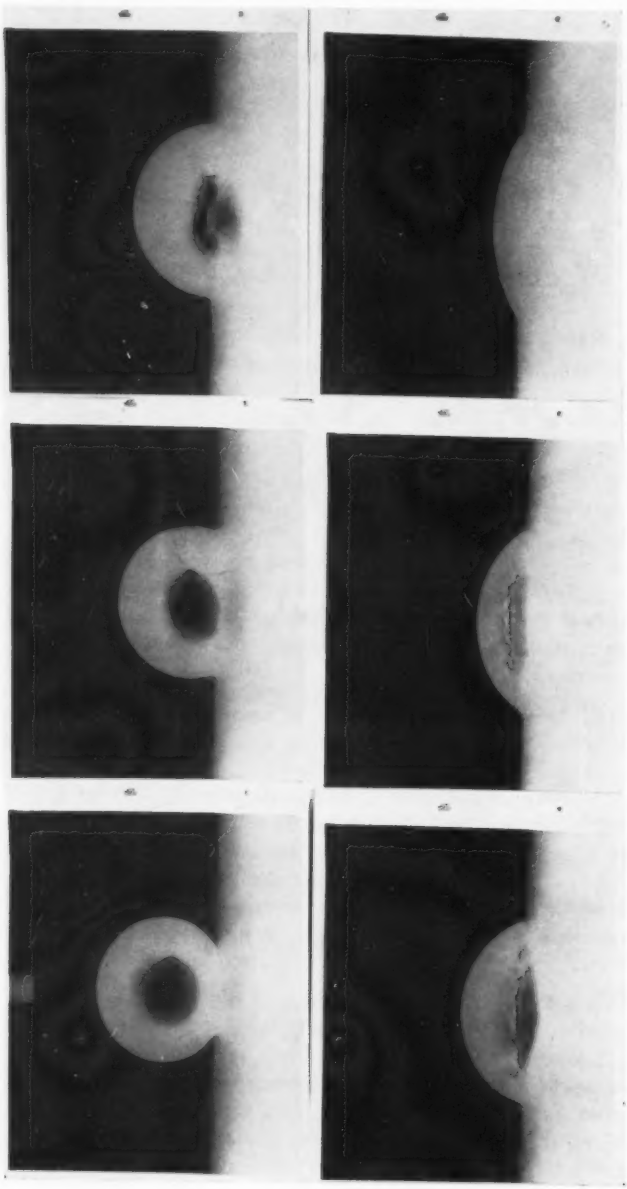

FIGURE 8.—Sequence showing absorption of a drop of water by side leather.

Relationship between volume changes and contact angle changes.—A typical graph of the penetration rate of water into a piece of snuffed-grain chrome-tanned side leather is shown in Fig. 9. The curve

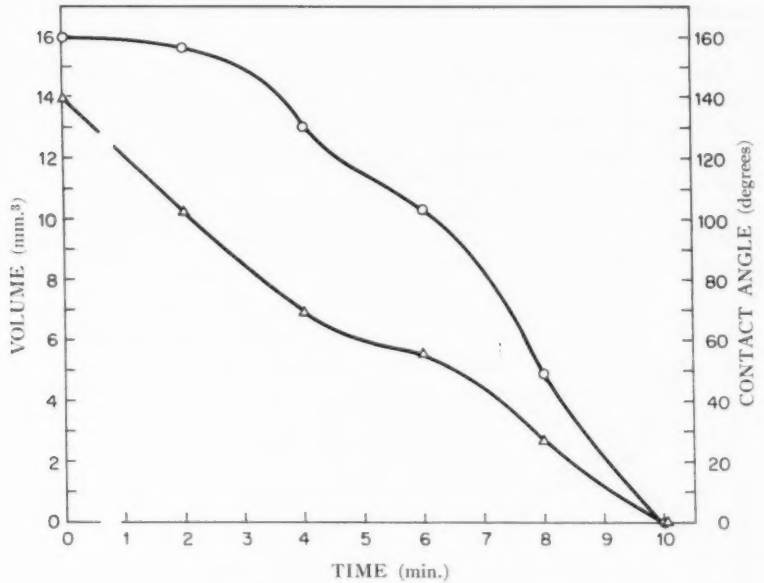

FIGURE 9.—Rate of change of contact angle and of volume of a drop of water on snuffed-grain side leather at 70° F. and 65% R. H.

○ Volume
△ Contact angle

showing the volume of the drop remaining on the surface at varying time (t) is plotted on the same graph as the curve showing change of contact angle with time. The rate of change of the contact angle is much faster than that of the volume in the early stages. However, the two curves soon follow similar courses. This has been true in all our work to date and has led to our use of rate of change of the contact angle as a measure of penetration rate rather than the change of volume. The calculation of contact angle is an easier process mathematically because of its simpler formula and also because, being a simple ratio, the measurements taken from the photograph can be used directly for the calculation. In calculating volume, since the formula employed is a cubic equation, it is necessary to determine the exact magni-

fication and calculate the volume in the original units.* The slight hump on the two curves is significant. It is found repeatedly and usually has been found to be beyond the experimental errors of the measurement (<2.5%). We are uncertain of the cause but believe it to be due to increased resistance to penetration which is encountered when the hair follicles have been filled with water.

Area location variations.—The effect of area location variation on water absorption in side leather has been studied. Studies were made on both full-grain and corrected-grain leathers from the same tannery. As was to be expected, for similar locations penetration rate was slower in full-grain than in corrected-grain leathers.

Area variations in penetration rate were considerable. An important finding was that penetration was fastest in the areas of the highest angle of weave of the fibers. This is illustrated in Fig. 10. It can be seen that in the

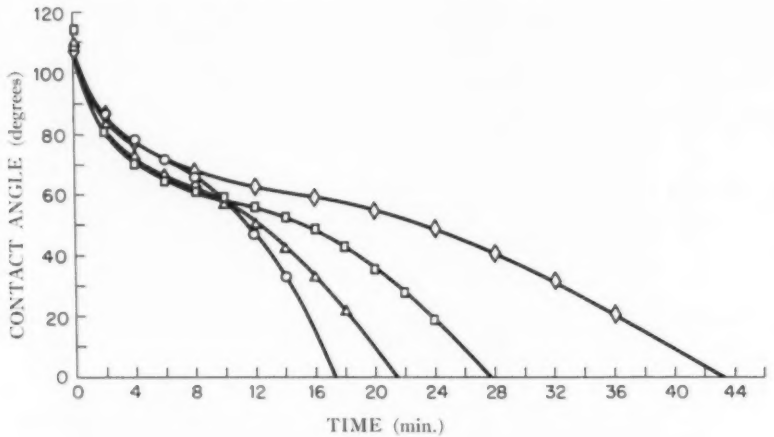

FIGURE 10.—Absorption of deionized water in various areas of full-grain side leather as indicated by change of contact angle with time. Saturated atmosphere.

○ Rear of bend near backbone
△ Butt
□ Right foreleg
◊ Mid-belly

butt and in the rear portion of the bend region near the backbone where the angle of weave is high (12, 13) the penetration rate is faster than in the belly and the foreleg where the fibers are tightly packed and lying predominantly in a plane parallel to the leather surface. The determinations made for

*Since this was written, Dr. E. W. Miller, of our laboratories, has noted that reversion to the original units is not required if apparent volumes are calculated and percent changes in these are computed and plotted.

this graph were made on full-grain chrome-tanned side leather and were run in a saturated atmosphere so that there is no effect due to evaporation. The graph for similar areas of snuffed-grain leather was much the same except for a shorter time axis. The points shown are the average of those from at least two and usually three runs. Agreement was good between runs made in the same area. Therefore, formulations can be compared on small pieces from the same area of the hide by this technique.

In spite of the large variation in penetration rate from area to area, there was surprisingly little variation in the initial contact angle. From a study of 31 different sections of a full-grain side leather the average initial angle of contact was found to be 111.0°, and the standard deviation was only 5.39°.

Corrected-grain leather showed slightly more variation, as was to be expected because of minor variations in buffing. Nevertheless, it was surprisingly uniform. The initial angle of contact for 23 different areas was 136.7°, and the standard deviation was 7.51°.

The difference in initial angle of contact between full-grain leather and a snuffed-grain leather is significant. The full-grain surface is more easily wet. This helps to explain the better flow-out of finishes on this type of leather. The higher contact angle on the roughened surface tends to support the concepts of the British workers (9, 11) concerning the importance of a grid-like network of fibers in raising the effective contact angle.

Some important practical conclusions to be formed from these data are as follows.

1. All other things being equal, flow-out will be better on full-grain leather than on corrected leather.

2. Those areas of the hide where penetration rate is slow will go into the tannery drying oven still wet, leaving a thicker film on the surface in those areas.

3. This will tend to have a leveling effect, because this thicker film will be deposited on the so-called "hungry" areas of the hide.

4. In doing experimental work with finishes, comparisons of finished leather pieces from different areas of the hide should be made with great caution.

Comparison of finish formulations on leather.—As we have seen above, it is possible to compare two finish formulations for their behavior on leather using the penetration rate apparatus, provided the leather pieces are selected from the same area of the hide. It is advisable to run controls with water to obtain the effect of hide characteristics, since these may vary somewhat with the amount and kind of fatliquor employed, depth of buffing, etc.

The best method of showing the utility of the apparatus in determining finish characteristics is to show a direct comparison of the data on two quite different finishes and how they correlated with the characteristics of the two finishes in actual applications. The data on two such finishes tested on chrome-tanned side leather are shown in Fig. 11.

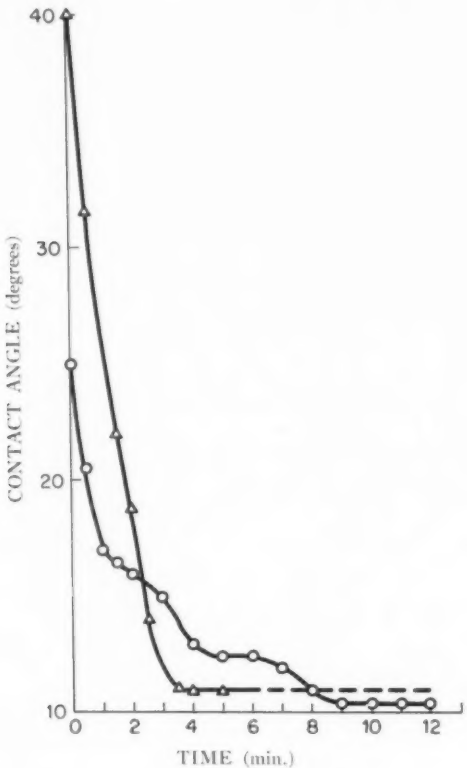

FIGURE 11.—Rates of penetration of two different finish formulations on snuffed-grain side leather as indicated by changes in contact angles.

△ Finish A
○ Finish B

It can be seen in this figure that Finish A does not wet the surface of the leather as readily as Finish B. Finish A's penetration into the leather was extremely rapid—in fact it was almost the same as that of water, since the

water control in this series was shown to have a rate of change, $d\theta/dt$, of approximately 13.5 degrees/minute. It was thought that this rapid penetration rate for Finish A might not have permitted proper packing of the emulsion particles in order to make a good continuous film. Brown (6) has brought out the importance of this phenomenon in his paper on film formation. Microscopic examination of leathers swabbed with Finish A was conducted by the methods described in this report and revealed that this was indeed the case. Although the pigment contents of Finish A and Finish B were approximately the same, the pigment layer at the surface of Finish A was thicker and more porous than that of Finish B. It was concluded that the deposition of Finish A had occurred by a flocculation type of phenomenon.

Finish B, on the other hand, had much different characteristics. Because of its lower initial angle of contact, its initial flow-out was better than that of Finish A. This was particularly noticeable in spray applications. The penetration rate of Finish B was similar to that of water and of Finish A for the first minute. Then there was a sudden slowdown followed by a more pronounced slowing of the penetration rate. Later studies showed that Finish B had a large increase in viscosity for a relatively small change in concentration, and this undoubtedly played a role in the slowing of its penetration rate. Because of this slowing, the emulsion particles had plenty of time to pack, and a good, tough, continuous film was formed which packed well and lay closer to the surface than the film from Finish A. This is determined not only from the microscopy but also from the higher contact angle (or volume, if preferred) of Finish A at the conclusion of the penetration rate studies as shown in the figure.

As a result of these differences in height and structure of the films on the surface, it was found that Finish A had greater covering power than Finish B, but Finish A tended to be less abrasion-resistant than Finish B and in fact had some "chalky" character. Tightness to wet-rubbing was better in Finish B, and it tended to follow more closely the contours of the surface, giving a more "natural" look on full-grain leathers.

An interesting feature was the difference in "streaking" characteristics of the two finishes. If both were applied with a relatively dry swab and swabbed off rapidly, there was more tendency for Finish A to streak by being worked while it was becoming relatively dry. However, if both were applied with a relatively wet swab (or brushed on with a seasoning machine) and the excess was wiped off, there was a tendency on the part of the swabber to wipe off the leather finished with Finish B for a longer period because of its wetter appearance. In doing so, he worked it during the period when its viscosity had increased to the point where it did not flow together properly, so that streaking resulted. Finish A, on the other hand, behaved well under these conditions.

The practical significance of the findings in this section can be summarized as follows:

1. To get good flow out, particularly in spraying, use of materials with a low angle of contact is indicated.

2. If coverage is the primary object, this can be achieved best with materials whose penetration rate is fast.

3. If toughness and tightness are desired, a slow penetration rate is indicated.

4. By the usual methods of swab application, materials with a slow penetration rate are liable to streak, if the reduced rate of penetration is due to an increase in viscosity.

Relationship between penetration rate and penetration depth.—In view of the differences in penetration rates for finishes A and B, it was of interest to us to study the depths of penetration of the binders from these two finishes. This was done microscopically on cross sections of swab-finished leathers which had been stained by the phenylhydrazine technique. Measurements were made with a screw micrometer eyepiece previously calibrated against a standard through the same microscope objective. The depths of penetration were measured at five or more areas along the section, excluding the hair pockets. These were averaged, and the standard deviation was computed. Thus the standard deviation serves as a measure of variation along the section.

Finish	Depth of Binder Penetration	Standard Deviation
A	561 microns	65 microns
B	559 microns	65 microns

These differences in finish penetration were not significant. Hence, a difference in penetration rate does not necessarily produce a change in depth of penetration.

The depths of penetration noted above were greater than we usually find. In most systems penetration is less than 300 microns. However, this, of course, varies depending on the nature of the binder and the type of leather, as well as other factors, all of which we have not yet fully resolved.

SUMMARY

An apparatus has been developed for following the rate of penetration of liquids into porous surfaces by photographic semimicro techniques. The rates of penetration of various leather finish formulations have been determined accurately by this procedure. Studies can be made on single drops of

finish formulations. Variations in rate of penetration in various portions of the hide have been studied. In addition, the wettability of the leather by the finish and the final height of the finish on the leather surface can be easily determined from the same series of measurements.

By the use of the microscope and some simple histological staining techniques, the final depth of penetration of the pigment and the binder portions of finishes were determined. The final depth of penetration of a finish does not necessarily coincide with its rate of penetration. The penetration characteristics of pigment and binder are very dissimilar.

The apparatus for measuring penetration rate was described. The practical significance of the findings was discussed.

ACKNOWLEDGMENT

The authors wish to acknowledge the generous reporting by H. Hatton and A. Schurr of their experience in practical swabbing applications with the formulations tested. These reports, together with our own swabbing experiences, enabled us to make the correlations between basic information and practical applications.

Comments and suggestions made by Dr. Harold L. Greenwald were helpful in setting up the apparatus for measuring penetration rates and contact angles.

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REFERENCES

1. Burkart, C. A., N. D. Gallagher, and M. B. Neher. *JALCA*, **51,** 418–28 (1956).
2. Vely, V. G., N. D. Gallagher, and M. B. Neher. *JALCA*, **52,** 622–33 (1957).
3. Amos, G. L., and G. W H. Thompson. *J. Soc. Leather Trades' Chem.*, **41,** 23–32 (1957).
4. Cheronis, N. D. *Shoe and Leather Reptr.*, **283,** No. 7, 26–8 (1956).
5. O'Flaherty, F., and J. Tancous. Personal communication.
6. Brown, G. L. *J. Polymer Sci.*, **22,** 423–34 (1956).
7. Glasstone, S. *Textbook of Physical Chemistry* (New York: Van Nostrand, 1940) 474–75.
8. Mack, G. L. *J. Phys. Chem.*, **40,** 159 (1936).
9. Beakbane, M. E. *Progress in Leather Science* (London: British Leather Manufacturers Research Association, 1948) Chap. 15.
10. Buechler, P. R., and R. M. Lollar. *Quartermaster General's Research Reports on Leather Technology*, Jan. 15, 1948.
11. Cassie, A. B. D., and S. Baxter. *Trans. Faraday Soc.*, **40,** 546 (1944).
12. O'Flaherty, F., W. T. Roddy, and R. M. Lollar, editors. *The Chemistry and Technology of Leather* (A. C. S. Monograph No. 134. New York: Reinhold Publishing Co., 1957) Vol. I, pp. 14, 34.
13. Conabere, G. O. *Progress in Leather Science* (London: British Leather Manufacturers Research Association, 1948) Chap. 2.

DISCUSSION

DR. M. M. BALDWIN (Battelle Memorial Institute): In reading this paper I got the reaction, which I think you will all agree with, that it is always a good idea to work to get as clear a picture as possible of what is really happening in processes in which you are interested. These two general techniques have, I believe, been used in various areas of scientific investigation, and it is gratifying to see them applied here to the finishing process. The paper we have just heard should lead to a better understanding of what goes on when a finish is applied to leather. I think, also, a study of the behavior of drops of various kinds of liquids on leather might lead to additional understanding of variations and what happens in leather treatments.

To start out the questioning I would like to ask Dr. Buechler a two-phase question. In his comparison of finishes A and B, does he have any data on the physical properties of these finishes—that is, how they differ from one another? And since I suppose he has looked at a variety of leathers in his work, would the behavior of these finishes vary from lot to lot or among different leathers?

DR. BUECHLER: Well, of course we made up finish formulations so that we did know their compositions, and we made comparisons. We have not tied down all the variables yet. What we are doing is changing the components in the finish, one by one, and studying the effect of variations in the particular components.

One thing we did which would slow down the rate of penetration so that there was time for the molecules to pack, was to put in a water-soluble polymer which tends to thicken the formulation as the water is absorbed. You get an apparent difference in rate. Even though some of the polymer goes into the surface, enough of it still stays in the droplet so that, as the water goes in slightly faster, it increases in concentration, and of course, as the polymer concentration in the solution goes up, it does increase the viscosity and bring about this slowing effect.

There are other factors, but we have not tied them all down yet.

With regard to the second part of the question, we found a surprisingly good agreement between leathers from different lots from the same tanner, if we chose the same area each time for making a comparison. There were variations but not nearly as much as we had thought there would be. On the other hand, when we studied similar areas in leathers from different tanners, we did find considerable differences, and right now we are working out techniques for determining the reasons for those differences.

DR. BALDWIN: I imagine that on initial wetting you had perhaps quite a difference in surface tension of the two finishes?

DR. BUECHLER: We have found that lowering the surface tension of the finish is another way to lower the contact angle. This can be done by adding more of an emulsifier so that you have more excess emulsifier in the system.

DR. SELIGSBERGER (Q. M. Research and Engineering Center): Does the stability of the finish have anything to do with the pH of the leather? How do competitive finishes compare in this respect?

DR. BUECHLER: You are asking a very general question. Of course we like to think that our own finishes are extremely stable, and we have found them to be so. With regard to competitive finishes, I don't know. We have compared our finishes with other finishes on leather with pH as low as 2 under unusual circumstances. We have applied them—this is chrome side leather I am talking about—at pH values around 4, and our emulsions are stable enough so that they hold up. I have not followed this out with the new technique yet. It is just a tool we have not fully utilized as yet.

DR. GEORGE VON FUCHS (Wallerstein Corp.): Have you studied the effect of oil on the leather surface?

DR. BUECHLER: This is what I think is largely responsible for the differences between tanneries. We are working out a semimicro technique so that we analyze just the surface layer for oil content.

JOHN HEILER, JR.: I believe there will be a difference in the results of your tests if the temperature of the solution of the finishes or the temperature of the leather is changed.

DR. BUECHLER: That may be. As I mentioned, to eliminate any such differences and to get valid comparisons we have been working in a constant temperature room at 65% relative humidity, or else a saturated atmosphere. We found little difference actually between the two conditions if the leathers were not preconditioned. But when we utilized the saturated atmosphere, we usually preconditioned our leathers in a saturated atmosphere by putting them in a desiccator over water. This does slow down the penetration because there is already some water in the specimen.

DR. VON FUCHS: You mentioned that if you have difficulty lowering the contact angle, you add more emulsifying agent. Does this additional emulsifying agent affect the water resistance of your finish adversely?

DR. BUECHLER: We have not been testing much for water resistance. Most side leather tanners are not too interested in that property except for military and workshoe use.

DR. VON FUCHS: How about things like water-spotting or crocking when rubbed with a wet cloth?

DR. BUECHLER: We do test for crocking, but this is just a base coat. I am interested in what happens in the base coat when you put it on. The top coat takes care of the resistance to crocking and to water-spotting.

DR. VON FUCHS: Another question: Could part of the wetting be accomplished by a volatile polar compound like isopropyl alcohol which will evaporate and not leave a harmful residue?

DR. BUECHLER: This can be done, and I understand some finishes do contain some of that in their formulation.

DR. MANN (Q. M. Research and Engineering Center): I have one suggestion which might tend to eliminate part of your variability. You are putting a drop on the leather surface, and it is not wetting for several minutes. Now, in actual practice, when applying the finishing material, you do what we do when we measure water resistance of glove leather—you apply force to the leather. You might be able to modify your technique slightly by applying pressure, perhaps with a metal or glass rod, and possibly improve the reproducibility.

DR. BUECHLER: First of all, we have found the initial contact angles to agree extremely well when you consider that in 31 areas of the surface we found angles of approximately 111 degrees with a standard deviation of only 5.4 degrees. I think that is rather remarkably good agreement over a hide.

DR. MANN: I was not questioning the reliability of results but questioning whether a static method would correspond to the dynamic method of rubbing and swabbing as used in the application of finish.

DR. BUECHLER: I know, but we have been correlating this with actual dynamic methods. Actually it may have been misleading to show you the disappearance of the water drop on the surface. Finish formulations are generally of much lower initial angles of contact, usually between 30 and 40 degrees, so that they do wet the surface very readily.

DR. BALDWIN: Maybe we could stick the leather on an ultrasonic plate.

LIFE LINES

Brief Biographies of Our Contributors

Dr. Peter R. Buechler received his Ph.D. from the University of Cincinnati for graduate work at the Tanners' Council Laboratory. He served as Research Associate and Assistant Professor with the University of Cincinnati on the staff of the Tanners' Council Laboratory and as Director of the Surgical Chemistry Laboratory. He has also been a consultant for the U. S. Veterans Administration and for Johnson and Johnson. He was a Senior Scientist for Olin Industries before and during their merger with Mathieson to form the present Olin-Mathieson Chemical Corporation., and was General Manager and Assistant Secretary-Treasurer of the Tanners Research Corporation of New Jersey prior to assuming his present position with Rohm & Haas Company.

Stanley C. Chmielewski serves as the Rohm & Haas Company's Research Division photographer at the Philadelphia laboratories. His eight-year employment with the company was interrupted by a three-year tour with the U. S. Navy as an Aviation Photographer's Mate. Previous employment included color photographic printing and commercial photography. In addition to service training, Mr. Chmielewski attended the Winona School of Photography. A director of the Society of Commercial Photographers of Philadelphia, he is also active in the Naval Reserve and the Industrial Division, Professional Photographers of America.

Ira D. Clarke is a graduate of Butler College, Indianapolis, Indiana. He retired in 1957 after 40 years with the U. S. Department of Agriculture, first in the Leather and Paper Laboratory of the Bureau of Chemistry in Washington and from 1941 on in the Hides, Tanning Materials, and Leather Section of the Eastern Utilization Research Laboratory in Philadelphia. An ALCA member since 1920, he has been the author or coauthor of dozens of contributions to *JALCA*. Even in his well-earned retirement he continues to serve us as abstracter of *Das Leder*.

Dr. Theone C. Cordon—See the October, 1958, *Journal*.

Ernest R. Jones has been a research chemist with the Rohm & Haas Leather Department in Philadelphia since June, 1957. He is a recent graduate of Brown University where he specialized in analytical chemistry. Previous leather experience included summer employment with Richard Jones & Co., Inc., of Gloversville, N. Y.

DR. JOSEPH NAGHSKI—See the February, 1958, *Journal*.

DR. WALLACE WINDUS received his Bachelor's degree from the University of Montana and his Doctor's degree from the University of Illinois. He was employed by the Rohm & Haas Company from 1931 to 1944, during which period he was coauthor of several important papers on the mechanism of unhairing. He was then associated with John R. Evans and Company and the Tanimex Corporation. Dr. Windus joined the staff of the Eastern Utilization Research and Development Division of the United States Department of Agriculture in 1956 and is now Head of the Processing Investigations of the Hides and Leather Laboratory. He has been a member of ALCA since 1932 and has served as Councillor (1951–53).

Imitation of Sable Skins. Hamster skins closely resembling sable have recently been brought into commerce from England. The process of preparing them is as follows: A mordant prepared from 1 part of quicklime and 10 of water is applied with a brush to the fur side of the hamster skins and allowed to remain for 12 hours. The skin is then dyed with the following preparation: Pulverize and mix roasted gall-nuts 3 pounds, sal-ammoniac 4 ounces, sumach 15 ounces, sulphide of antimony 13 ounces, verdigris 2 ounces, iron cinders 10 ounces, copper ash 4 ounces, and clay 10 ounces. Compound the mixture with 12 gallons of water, stirring constantly. Apply a layer of this to the hamster skins, and after 24 hours place every 2 skins with the fur side together, let them again lie for 24 hours, and then beat them. Repeat the whole process until the desired color is obtained. The skins are finally cleansed by revolving them in a closed cylinder filled with sand and mahogany sawdust.
—*The Techno-Chemical Receipt Book*. Philadelphia: Henry Carey Baird & Co., 1903.

Heating the Liquor in Tanning. Hot liquor should never be used in tanning. Liquors of 70° to 80° F. may be used without harm in the last stages, when the leather is completely tanned. There has always been a doubt whether warm liquors improve the quality of the leather, it being possible that the process of tanning is somewhat facilitated thereby. The strength of the liquors and their frequent use facilitate tanning and increase the weight.
—*The Techno-Chemical Receipt Book*. Philadelphia: Henry Carey Baird & Co., 1903.

New Tanning Process. According to the process patented by *J. & C. Ballanchino*, and *H. Pronck*, of Berlin, the hides are treated with the following fluids: For solution No. 1, 20 to 30 parts of chromate of alumina are dissolved in 20 to 30 of wood vinegar, and diluted with water to 1000 parts. For solution No. 2, a concentrated solution of tartar is compounded with some ammonio-nickel chloride dissolved in ammonia. The skins, carefully freed from lime, are then placed in a mixture of 2 parts of the first and 1 of the second solution, 18 to 21 days being sufficient for thick bullock hides.
—*The Techno-Chemical Receipt Book*. Philadelphia: Henry Carey Baird & Co., 1903.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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NOTICE TO CONTRIBUTORS AND ABSTRACTERS

Effective immediately, all manuscripts submitted for publication, all abstract copy, and anything else that should receive the attention of the Editor-in-Chief should be mailed to Dr. Wallace Windus, Editor-in-Chief, 1437 Bryant Lane, Meadowbrook, Pennsylvania.

EDITORIAL

With this issue of the *Journal* the editor-in-chief changes from Dr. Henry B. Merrill to Dr. Wallace Windus. In accordance with the action of Council in 1955 the editor now serves a term of three years. The new editor wishes to acknowledge the kindness of Dr. Merrill in being responsible for this issue of the *Journal*.

No fundamental change is contemplated in the character or objectives of our *Journal*. From the time of the publication of the first issue in January, 1906, it has served leather chemists well. Many discoveries and developments have been printed in its pages for the first time. As leather chemistry expanded from sole leather to include every branch of the industry the Association and *Journal* have grown to meet new requirements. The rapid development of the chemical industry after the First World War has added new dimensions to our science. Industry-sponsored and government laboratories have been established and have contributed more than their share of publications. Today our *Journal* stands as one of the leading industry journals of the world.

The incoming and outgoing editors agree that it would be very desirable to increase the proportion of manuscripts received from chemists working in tanneries. The editors are aware of the difficulties. However, applied research is being done in the leather industry which need not be confidential and which could be completed in a form suitable for publication. This would strengthen our *Journal*. The chemists concerned are in the best position to know the specific problems that have been solved. The editors invite them to take the initiative in submitting papers for consideration.

Review articles will continue to be published. These will be written by authorities in specialized aspects of chemistry directly or indirectly related to leather. In view of the great increase in the knowledge of the structure of collagen in recent years it is hoped that some papers on this subject can be obtained.

Nearly everyone is aware of the tremendous amount of time and effort that Dr. Merrill has spent on the *Journal* and the fine job he has done. The present editor hopes to be able to follow, in some measure, his excellent example. In this endeavor he will have the substantial help of the associate editor, the managing editor, the editorial board, and the abstracters.

Your editor is gratified to have the continuing assistance of Dr. Thomas C. Thorstensen as associate editor and Earl J. Watt as managing editor. Dr. Thorstensen is available to answer the technical questions of the managing editor quickly. He also served as acting editor in Dr. Merrill's absence in Europe in 1957. Mr. Watt ably relieves the editor of all but the technical

aspects of editorial matters. These duties have increased with the growth of our *Journal* and will no doubt continue to expand.

The editors wish to express their appreciation to the editorial board and to the abstracters. The members of the editorial board serve without remuneration and devote considerable time to reviewing manuscripts. They frequently offer constructive suggestions for the improvement of a paper. The abstracters receive a nominal remuneration for their efforts in keeping us abreast of the current literature.

W. WINDUS

EMPLOYMENT

FINISH SALESMAN WANTED. Established medium-size manufacturer of leather finishes, pigments, etc., has opening on sales staff. Prefers man with recognized background in finishing and willing to travel. Guaranteed salary plus commission and expenses. Replies held confidential. Send replies to Box F259, c/o Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES

Tentative Program—Munich Conference

Sunday, Sept. 6, and Monday, Sept. 7—Meetings of the Executive Committee and the International Commissions

Monday, Sept. 7

Morning: First meeting of delegates

Afternoon: Sightseeing tour

Evening: Reception

Tuesday, Sept. 8

Morning: 9:30. Official opening in the Herkulessaal der Residenz; welcome addresses, and the Harvey Memorial Lecture by Professor Burton.

Afternoon: Lectures on collagen

Wednesday, Sept. 9

Morning: Miscellaneous papers

Afternoon: Papers on aldehyde tanning

Evening: Bavarian Evening in the Hofbrauhaus

Thursday, Sept. 10

Morning: Miscellaneous papers

Afternoon and evening: Trip on special train and ship to the Castle "Herrenchiemsee" with festival illumination and concert

Friday, Sept. 11

Morning: Papers on vegetable tanning and combination tanning with chrome

Afternoon: Free. There is the possibility of a city sightseeing tour.

Evening: Gala Evening

Saturday, Sept. 12

Morning: Miscellaneous papers. Second meeting of delegates. Conclusion of the Congress.

ABSTRACTS

The Production of Chrome-Vegetable-tanned Leathers. L. Kucka and M. Minarik. *Veda a Vyzcum v Prumyslu Kozedelnem*, **3**, 79–88 (1958).—Four types of Cr-vegetable tannage are distinguished: (1) pretannage with 0.5–1.0% Cr_2O_3 and retannage with vegetable tannins, or tannins plus syntans, for sole, mechanical, and heavy upper leathers; (2) pretannage with 1.2–1.8% Cr_2O_3 and retannage with syntans, or syntans plus vegetable tannins, for fancy and lining leathers; (3) pretannage with vegetable tannins and/or syntans, and retannage with Cr salts, for specialties such as shrunken grain leathers; (4) pretannage with syntans, tannage with Cr salts, and retannage with vegetable tannins and syntans for pasted side upper leather. Of these the first is the most questionable, although it is used exclusively in USSR for tanning sole and heavy upper leathers. In other countries its use has been limited because of several drawbacks. It was tested on the pilot-plant scale, 90–100 hides daily for 2 years, at the SVIT tannery. Delimed hide is pickled in a drum for 8–10

hr. with 100% water, 1% H_2SO_4, and 8% NaCl. A Cr liquor, 40% basic, containing 0.5–0.8% Cr_2O_3 is added to the spent pickle. The hides are drummed 16 hr. with 10 hr. movement. The basicity is regulated with Na_2CO_3 or Na_2SO_3. Tannage is done in 1 or 2 drums with 29% tannin consisting of 80% oak wood extract and 20% syntans. The tannage in 1 drum lasts 2 or 3 days, with 140% liquor, the temperature rising from 22° to 40°C. Fresh extracts are added to the liquor for the next lot, and the liquor is drained after 3 or 4 lots. The 2-drum tannage is started in a used liquor, and the hides are transferred to a 45° liquor in the second drum. The total time is again 3 days. The drums do not have hollow axles and are filled to 75% of capacity. The best procedure was found to be: soaking 2 days with antiseptic; breaking on unhairing machine or by drumming; liming in 4 pits, with 0.1% and 0.6% Na_2S in the first and second pits and pure CaO in the third and fourth, at 22°C., 500% liquor, one pit sewered each week; fleshing, unhairing, and light splitting; deliming at not over 25°C. with 2% NH_4Cl for 2 hr. till the pH in the center of the hide is 8.5–9.0, which is preferable to the USSR practice of deliming to pH 8.0–8.5 using more NH_4Cl and a longer time; pickling with 170% water, 10% NaCl, 2% HCl for 4 hr.; adding 6% $KCr(SO_4)_2 \cdot 12\ H_2O$ (0.85–0.90% Cr_2O_3) to spent pickle; drumming 5–6 hr., then adding 0.5% Na_2CO_3, drumming 90 min., standing 12 hr., adding of 0.5% more Na_2CO_3, drumming 90 min.; horsing 24 hr. Drainage of chromed stock should be complete as Cr liquor from hides forms much sludge with vegetable tannins. The spent Cr liquor contains 0.5–0.9 g. Cr_2O_3 per l.; pH 4.5. The leather contains 0.8–1.0% Cr_2O_3; more would make sole leather too soft, though it would raise the shrinkage temperature. This is more suitable for upper leather. The retannage with vegetable tannin and syntans has been thoroughly tested. It was found advisable to transfer the prechromed hides to a vat of weak tan liquor, then pass them through 3 suspender liquors, and complete the tannage in 2 drums.

	°Bk.	pH	g. tannin per l.
weak liquor vat	7	3.6	7–9
1st suspender	25–28	3.8–4.0	19–23
2nd suspender	30–35	3.8	30–35
3rd suspender	45–50	3.6–3.7	45–50
1st drum: when skins enter	70–80	3.6–3.7	100–120
when skins leave	50–60	3.6–3.7	55–65
2nd drum: when skins enter	90–100	3.6–3.7	150–180
when skins leave	70–80	3.6–3.7	120–140

Liquor from the weak liquor vat is drained daily. Tannin lost is 3.5–4.0% of the total given, compared to 2.3–2.8% for straight vegetable tanning and 6.5% in the purely drum tannage. The physicomechanical properties of Cr-vegetable sole leather are not much different from straight vegetable sole. Tensile strength is about 10% lower but complies with the standard. Hydrothermal stability is 90–100% compared to 75%. Resistance to wet abrasion is higher, but resistance to dry abrasion is lower. The production cycle was shortened from 86 to 39 days, but the change to the new system would require an investment that would not be regained. Cr-vegetable sole leather creates some difficulties in shoe factories, especially with Goodyear welt shoes. Cr-vegetable tannage of upper and lining leathers is decidedly better than straight vegetable tannage.

L.M.

Phase Transitions in Collagen and Gelatin Systems. P. J. Flory and R. R. Garrett. *J. Am. Chem. Soc.*, **80,** 4836–45 (1958).—The transformation of native beef Achilles tendon and rat tail tendon in admixture with ethylene glycol to the amorphous shrunken state has been investigated over the range of volume fraction, v_2, of collagen from 0 to 0.83. Precision dilatometric methods employed for $v_2 > 0.08$ revealed small but unmistakable latent volume changes (about 5×10^{-3} cc. per g. of collagen). The transformation is partially reversible, the latent volume change being slowly recovered in part upon cooling. Return to the previous liquidus occurs within $\pm$ 2°C. of the original transformation temperature T_m. These observations show conclusively that the transformation is properly represented as a phase transition, involving melting of crystalline regions, rather than as rate process. Melting temperatures, T_m, have also been ascertained by polarizing microscopy and, at high dilution, from the decrease in viscosity. The dependence of T_m on v_2 conforms rather well with polymer-melting theory, which yields 24 $\pm$ 5 cal. per g. for the heat of fusion of collagen. A glass-type transition observed both in native collagen-diluent mixtures below T_m and in shrunken dry collagen at 95°C. probably is associated with freezing-in of side chain disorder. Melting of gelatin gels resembles the remelting of collagen allowed to recrystallize by cooling after the initial transformation. The identity of the processes involved is indicated by the observation that T_m for gelatin-glycol is within 2°C. of that for collagen-glycol of the same composition. Author's summary

Ethylene glycol was chosen as the diluent in this work because solvolysis of collagen in water poses a serious obstacle to experiments on aqueous mixtures. H.B.M.

N-Terminal Amino Acids of the Constituent Proteins of Hides and Skins. K. Thomas Joseph and S. M. Bose. *Bull. Central Leather Research Inst., Madras,* **4,** 343–60 (1958).—The proteins used in this study and the methods by which they were prepared were: *Collagen* (Bowes and Kenten. *Biochem. J.*, **43,** 358 [1948]); *citrate-soluble collagen* (Orekhovich, reported by Bowes *et al., ibid.*, **61,** 143 [1955]); *soluble rat tail collagen* extracted with very dilute acetic acid; *neutral salt–soluble collagen* (Jackson, *ibid.*, **65,** 277 [1957]); "*modified*" *collagen* by treating collagen in 10% $CaCl_2$ solution brought to pH 10.5 with $Ca(OH)_2$ at 37°C. for 1 hr., which supposedly removes mucopolysaccharides; *elastin* from *ligamentum nuchae* by successive extractions with 10% NaCl, 0.15*M* Na_2HPO_4, and half-saturated lime water, washing with water, dehydrating with acetone and drying—making no attempt to remove collagen because it was assumed that the latter does not contain enough N-terminal amino acids to affect the results; *reticulin* from lymph nodes and from adipose tissue of skin (Bowes and Kenten, *Biochem. J.*, **45,** 281 [1949]); *reticulin* from rat spleen (Ottaway, *ibid.*, **58,** viii [1954]); *wool* by removing tips, washing, and extracting successively with ether and ethanol; *myosin* from rabbit muscle (Tsao, *Biochem. Biophys. Acta*, **11,** 368 [1953]); albumin, globulin, and mucoids from goatskin (Bose *et al., JALCA*, **50,** 192 [1955]). Collagen, the soluble collagens, elastin, myosin, and reticulin were dinitrophenylated by Sanger's method (*Biochem. J.*, **39,** 507 [1945]); wool by the method of Fritze and Zahn (*Proc. Intern. Wool Textile Research Conf.*, Vol. CPC, 119 [1955]); albumin, globulin, and mucoid by treatment for 2, 5, and

12 hr. respectively in 1 volume of 1.5% $NaHCO_3$ and 2 volumes of 2.5% dinitrofluorobenzene (DNFB) in ethanol, adjustment to pH 2 with HCl, extraction with ether, and washing the insoluble DNP proteins with water, absolute ethanol, and ether. The DNP proteins were hydrolyzed by refluxing with 12*N* HCl for 3 hr., except in the case of wool, which was heated in a sealed tube at 105°C. with 5.7*N* HCl for 18 hr. The reaction mixture was extracted with ether, the ether layer was washed 4 times with very dilute HCl, the ether was evaporated, the residue was dissolved in acetone and again evaporated, and the dinitrophenols were removed by sublimation. The ether-insoluble DNP acids were extracted with *n*-butanol from the aqueous phase from the ether extraction. The DNP acids were separated and identified by 2-way paper chromatography, first with *tert.*-butanol and benzyl alcohol (1:1) saturated with an equal volume of phthalate buffer solution at pH 6; second with a mixture of *n*-butanol and isoamyl alcohol (2:1) plus 10% of ethanol saturated with an equal volume of the pH 6 phthalate buffer. The DNP amino acids were determined by Fraenkel-Conrat's method. The unstable DNP derivatives of proline and hydroxyproline were looked for by the spectroscopic method of Phyllips (*Biochem. J.*, **60**, 403 [1955]) with negative results. The N-terminal amino acids found are given below, expressed as mmols. per 100 g. protein, uncorrected for losses.

Proteins	Aspartic Acid	Serine	Glycine	Alanine	Threonine	Glutamic Acid
Collagen	trace	trace	trace	none	none	none
Collagen $CaCl_2$-treated	trace	trace	trace	none	none	none
Collagen citrate-solube	0.11	0.05	none	0.04	none	none
Collagen neutral salt–soluble	0.03	0.035	none	none	none	none
Collagen soluble rat tail	0.07	trace	none	0.03	none	none
"Reticulin" (adipose tissue)	trace	trace	trace	none	none	none
Reticulin (rat spleen)	0.04	0.18	0.04	0.05	none	none
Reticulin (lymph node)	0.206	0.20	0.064	0.18	none	none
Elastin (*ligamentum nuchae*) containing collagen	0.04	0.05	0.05	0.09	none	none
Myosin	0.045	0.02	none	0.06	0.07	trace
Skin albumin	0.20	0.16	0.04	0.20	none	none
Skin globulin	0.32	0.43	0.05	0.34	none	none
Skin mucoid	0.33	0.35	0.05	0.20	none	none

The N-terminal acids found in wool (from Indian sheep) were aspartic, glutamic, serine, threonine, glycine, alanine, and valine. The amounts found agreed roughly with those reported by other workers, except that only 0.067 mmols. threonine per 100 g. wool was found, while others have found 0.24 to 0.48 mmols. The N-terminal amino acids found (as traces) in collagen are the same found by Deasy (*JALCA*, **53**, 203 [1958]) of whose work the present authors presumably were unaware. The agreement of the alleged reticulin of the adipose tissue with collagen seems to support the view that the supposed reticulin of skin is actually collagen. The authors point out that it is impossible to tell with certainty whether the small amounts of N-terminal amino acids found in fibrous proteins are to be attributed to the protein itself or to small amounts of low-molecular-weight impurities or degradation products. H.B.M.

Simple Microdetermination of Kjeldahl Nitrogen in Biological Materials. C. A. Lang. *Anal. Chem.*, **30**, 1692–94 (1958).—A simple method, using commonly available laboratory apparatus, has been developed which involves acid digestion, nesslerization, and measurement of the resultant color. Digestion is done with samples of less than 5 mg. with 0.2 ml. of a K_2SO_4-H_2SO_4-$SeOCl_2$ digestion mixture in 15 x 125 mm. borosilicate bacteriological test tubes. These are inserted in slanting holes in the cover of an electrically heated sand bath, so that the protruding part of the tube acts as a condenser. The sand bath is heated to 310°C. in about 1.5 hr., and digestion is continued 1 hr. longer. The contents of the tubes are nesslerized directly or after appropriate dilution, and the color is read with a colorimeter at 420 $m\mu$ for N less than 15 γ, and at 500 $m\mu$ for higher levels. Maximum color development is achieved in 10 min. in the dilution method and in 30 min. in direct nesslerization, and is stable for 1.5 to 2.5 hr. The method is applicable to samples containing from 1 to at least 1000 γ N. Nitrogen recoveries on refractory compounds were 95–100% for lysine, 90–91% for tryptophan, 97% for arginine, 98% for uric acid, and 100% for human serum albumin. About 40 digestions can be made at once. H.B.M.

A New Method for the Manufacture of Picking Band Leathers. R. Selvarangan, Y. Nayudamma, and B. M. Das. *J. Indian Leather Technologists' Assoc.*, **6**, 142–45 (1958).—Heavy buffalo hides are soaked, washed, and limed 3 to 4 days with lime plus sulfide. After deliming with $(NH_4)_2SO_4$ the skins are either pickled with Calgon and acid or else pickled in the usual way and depickled with $Na_2S_2O_3$. They are then tanned with 12% of Al sulfate, 33% to 66% basic. The spent liquor has a pH of 4.2–4.5. Neutralization may be done with Na_2CO_3. The leather is fatliquored with a blend of sulfated fish oil, raw fish oil, soap, and a little borax, set out, and stuffed with a blend of tallow, fish oil, and a little sulfated fish oil. The stuffed leather is retanned with 7% to 10% vegetable tannin on the limed weight. The product is referred to as aluminum-oil-vegetable tanned. Practical tests on picking bands indicated that leather thus manufactured compared favorably with other picking band leathers with respect to useful life and tensile strength. Retannage with a mild vegetable tannin like babul gave higher tensile strength but greater stretchiness than retannage with astringent tannins like cutch and quebracho. This process is still in the pilot-plant stage. H.B.M.

The Proteins of Animal Skins. I. J. P. Danby. *Leather Trades Rev.*, **127**, 383 (1958).—The author classifies proteins into two groups, fibrous and nonfibrous. He breaks down these proteins into four subgroups characterized by high contents of (1) glycine, (2) aspartic and glumatic acids, (3) lysine and arginine, and (4) proline and hydroxyproline. All the known proteins in nature are constructed from little more than 20 amino acids. Amino acids he classifies into four main groups: (1) those having side chains which are chemically inactive (nonpolar), (2) those having chains which are chemically active (polar), (3) those having chains possessing a hydroxy group, and (4) those containing sulfur. Skin collagen contains relatively high proportions of two acids which are not strictly amino acids, namely, proline and hydroxyproline. In the collagen molecule, 3 in 10 of the building units are glycine,

about 3.5 in 10 are units other than glycine and without chemical reactivity, and about the same proportion are polar and capable of chemical reaction. **II.** *Ibid.*, **128,** 21 (1958).—Proteins are described as chains of amino acids joined through peptide links. The investigations to establish the structure and molecular weight of protein are explained. **III.** *Ibid.*, **128,** 449 (1958).—This article discusses the collagen molecule and the importance of hydroxyproline as a constituent of this molecule. Shrinkage temperature is mentioned as a convenient method for determining the structural stability of the collagen molecule. J.J.

The Reaction of Zirconyl Sulfate with Collagen. K. H. Gustavson. *Svensk Kem. Tidsk.*, **70,** 367–78 (1958) (in English).—This is a general account of hitherto unpublished work, details of which are to be published elsewhere. The work was done with aged solutions of $ZrO(SO_4)\cdot Na_2SO_4$. Attempts to elucidate the complex composition of solutions of this compound led to rather ambiguous results because of the large size of the complexes, their great lability, and their tendency to precipitate. However, resin exchange experiments by the batch technique, paper electrophoresis, and free electrophoresis all indicated the presence of about 1/3 nonionic complexes and about twice as many anionic as cationic complexes. Tanning tests were carried out with hide powders, variously pretreated, tanned for 24 hr. at pH 1.6. The tanned powders were washed, but not neutralized, and analyzed for ZrO_2 and hide substance. From the effects of the various pretreatments on ZrO_2 fixation it is deduced that most of the tannage is accomplished by fixation of anionic complexes by the guanidyl group of arginine residues. Only a minor fraction of the Zr is fixed by carboxyl groups because esterified hide powder fixes 2/3 as much ZrO_2 as native collagen. Neither the ϵ-amino group nor the hydroxyl group is involved because exhaustive acetylation does not affect the fixation. The -CO-NH- linkage is not involved because (1) fixation is not increased by heat denaturization or pretreatment of collagen with 2*M* NaSCN, (2) little ZrO_2 is fixed by a polyamide copolymer of Nylon 66 and caprolactam, and (3) Zr leather resists the H-bond-breaking agent 8*M* urea. Fixation of ZrO_2 is greatly reduced by inactivation of ionic groups by naphthalene disulfonic acid and almost completely inhibited by the irreversible blocking of such groups by novolaksulfonic acid. Therefore, Zr is fixed by ionic groups, and since the ϵ-amino and carboxyl groups play only minor roles, it is concluded that fixation occurs through arginine residues. An apparent shift of the isoelectric point of collagen to the acid side after Zr tannage supports this conclusion. However, if this hypothesis is correct, then the anionic complex fixed at each guanidyl group must contain at least 4 Zr atoms to account for the large ZrO_2 fixation. H.B.M.

A Novel Type of Metal-Protein Compounds. K. H. Gustavson. *Nature* (London), **182,** 1125–28 (1958).—The compounds referred to are formed by treating collagen with very basic Cr perchlorate containing mostly nonionic Cr complexes, about $[Cr_2(OH)_5ClO_4]$. Evidence is presented to show that these complexes are fixed by the keto-imide group of collagen. Cr fixation from 33%-acid $Cr(OH)_2ClO_4$ solution is increased by heat-denaturization of collagen or pretreatment with 2*M* $HClO_4$, is little affected by esterification of COOH

groups of collagen which practically inhibits fixation of cationic Cr; and is practically inhibited by vegetable pretannage which blocks keto-imide groups. A polyamide resin containing few active groups other than -CO-NH- fixes nonionic but not cationic Cr perchlorate complexes. The shrinkage temperature of calfskin tanned with 33%-acid Cr perchlorate is 84°–86°C., about like vegetable-tanned leather. This very basic Cr perchlorate also resembles vegetable tannins in precipitating gelatin and polyvinylpyrrolidone, which cationic Cr does not. The isoelectric point of collagen, as determined by the dye technique, is not changed after fixation of nonionic Cr from 33%-acid Cr perchlorate. H.B.M.

Pretanning Processes for Manufacturing Different Types of Industrial Leathers. M. A. M. G. Kibria. *J. Indian Leather Technol. Assoc.*, **6**, 169–71 (1958).—Soaking, liming, deliming, bating, and pickling processes for picking band, belting, and lace leathers, made from cattle and buffalo hides, are given. Overliming, overdeliming, and overbating must be avoided to preserve maximum tensile strength. H.B.M.

Method of Preparation of Artificial Degras. J. K. De, P. C. Roy Choudhury, and S. K. Ghosh. *J. Indian Leather Technol. Assoc.*, **6**, 172–75 (1958).—Madras fish oil, acid value 9.5, I_2 value 115, was blown with air at 120°C. for periods up to 24 hr. Acid value rose to 12.8, and I_2 value dropped to 70; there was little change in these characteristics after 9 hr. Batches blown 9 and 12 hr., after neutralizing the fat acids formed by blowing, and incorporating water, contained ash 0.7%, H_2O 20–21%, total fatty matter 66.8%, free fatty acids 8.2%, unsaponifiables 11.5%, I_2 value 58. H.B.M.

A Physicomicroscopic Study of Picking Band Leather. B. C. Basu and S. K. Mitra. *J. Indian Leather Technol. Assoc.*, **6**, 176–86 (1958).—Tensile strength and stretch data for 22 specimens of picking band leather are compared with microstructural characteristics. The leathers include Cr, vegetable, and combination-tanned ox and buffalo hides. Good quality is associated with thorough lubrication, fine and uniform splitting-up of fiber bundles, low to medium angle of weave, compact bundle packing, full bundles, and large to medium radius of curvature of bundles. H.B.M.

Manufacture of Glazed Kid Leather by Combined One and Double Bath Tanning Method with Indigenous Materials. Process No. 1. J. C. Deb and G. N. Hore. *Bull. Central Leather Research Inst., Madras*, **4**, 442–49 (1958). **Process No. 2.** *Ibid.*, 489–95.—Two complete processes are described. In (I) the skins are soaked 2 hr., broken on the beam, washed, limed 3 days with Na_2S and lime, unhaired, washed and treated with just enough H_2SO_4 to remove excess sulfide, relimed 2 days with white lime, delimed with NH_4Cl, bated overnight, raising the temp. to 98°–100°F. on the following morning (pH 7.8–8.0), and pickled with NaCl and HCl. In (II) the beamhouse process is the same except that the skins are painted with Na_2S-$Ca(OH)_2$ paste, unhaired, washed with dilute NH_4Cl solution to remove excess sulfide, and relimed. In

both processes tannage is started with essentially zero basic chromic salts, (I) chrome alum, (II) molasses-reduced Cr sulfate, after which $Na_2Cr_2O_7$ is added to the same bath. Next morning the skins are transferred to the reducing bath, (I) $NaHSO_3$, (II) $Na_2S_2O_3$ + HCl. The bath is adjusted to final pH 3.5–4.0. Neutralizing, coloring, fatliquoring, and subsequent operations are conventional. H.B.M.

Physicochemical Investigations of Tannin Fractions Obtained from Fresh Babul Bark. Y. Nayudamma, A. Nagosiromani, P. J. Rajalakshmi, K. N. Shama Sastry, and D. Ramaswamy. *Bull. Central Leather Research Inst., Madras*, **4**, 429–41 (1958).—Fresh babul bark, freed from chlorophyl by extraction with $CHCl_3$, was extracted with ethyl acetate for 30 min. (Fraction IA) and 72 hr. (Fraction I). Each extract was evaporated and freed from gums by solution in methanol, filtered, re-evaporated, and freed from carbohydrates by solution in ethanol, filtering, and re-evaporation. Fraction I was further fractioned into an ether-soluble Fraction II and an ether-insoluble Fraction V. Fraction II was dissolved in acetone and treated with benzene, yielding a precipitate (Fraction III) and Fraction IV soluble in acetone-benzene. Acetylated and methylated derivatives of all fractions were prepared. Melting points (mostly decomposition points) of these derivatives are given. Each fraction was studied by 2-way paper chromatography with (1) 10% acetic acid and (2) *n*-butanol–acetic acid–water (4:1:5), developed with $FeCl_3$ and $K_3Fe(CN)_6$. Fractions IA and I yielded trails with some indications of 2 or 3 fairly well-defined spots. Fraction II gave 4, and Fraction III gave 2, well-defined spots. On paper electrophoresis all fractions gave 2 anionically moving spots. Spectrophotometric examination showed maxima at 278 mμ and minima at 252 mμ in all fractions. Treatment with $AlCl_3$ or borate buffer (pH 10) produced 2 peaks, with shifts of 6–8 and 26–36 mμ for $AlCl_3$ and of 10–14 and 28–39 mμ for the buffer. Acetylated derivatives gave practically the same results, which is taken to mean that acetylation of phenolic groups was incomplete. Methylated derivatives showed only one peak at 275 mμ, attributed to -O-CH_3, indicating complete methylation of all ionizable phenolic groups by diazomethane. These results indicate that the fractionation accomplished only partial separation of the components. Each fraction was analyzed for carboxylic acids and phenolic groups by nonaqueous titration in dimethyl formamide solution under N_2 with 0.1*N* CH_3OK using anodically polarized Pt and calomel electrodes, and by differential spectrophotometric titration (*JALCA*, **52**, 291 [1957]). The 2 methods gave somewhat the same values for carboxylic acids, but quite different values for activated phenolic groups. Fraction IA differed from Fraction I in containing no carboxyl groups; Fraction III contained much less carboxyl and somewhat more phenolic groups than Fraction IV. Findings confirm chemical evidence that babul tannin is a mixture of condensed and hydrolyzable tannins. H.B.M.

Sole Leather Tannage Using *Pithecolobium Dulce* Bark. M. K. Udaya Varma, E. C. Mathew, and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **4**, 479–88 (1958); cf. *JALCA*, **52**, 103, 350 (1957).—Laboratory-scale tanning tests were made with buffalo hide, using *P. dulce* bark alone or blended with myrobalans. Best results were obtained with 5 *P. dulce* to 1 myro-

balans. The leather is said to compare favorably with that tanned with wattle and myrobalans, but the latter was superior in resistance to abrasion and absorbed less water. H.B.M.

Improvements in Curing and Prevention of Skins and Hides. S. C. Nandy, S. N. Sen, and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **4**, 496–503 (1958).—Khari salt is said to be better than NaCl for dry-salting because it is less hygroscopic, but Khari salt is available only in limited quantities, and the earthy matter that it contains tempts the curers to adulterate the skins with yet more earth. A mixture of 45 parts sodium sulfate, 50 parts magnesium sulfate (degree of hydration of these salts not specified), and 5 parts $(NH_4)_2SO_4$ gave results at least equal to Khari salt when used for dry salting. A mixture of 40–50 parts NaCl, 35–40 parts sodium sulfate, and 10–20 parts $(NH_4)_2SO_4$ is said to give better results in wet-salting than NaCl alone, and to suppress halophilic bacteria. The function of the ammonium salt is to lower the pH value. Cf. Indian patents No. 56251 and 57886. H.B.M.

Preparation of Synthetic Tanning Materials. N. Viswanathan and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **4**, 450–55 (1958).—Two processes previously covered by Indian patents No. 52798–9 are described. The two general processes for making syntans are (1) sulfonating a phenolic compound and condensing the product with HCHO, and (2) the "novolak" process in which the phenol is first condensed with HCHO and then the product is sulfonated just enough to impart solubility. The procedures here described combine these general processes. One mole of phenol is condensed with 0.6–0.8 moles HCHO at 90°–100°C. in the presence of 0.25–0.5 ml. H_2SO_4 dissolved in 12–20 ml. water. The product is separated from the water of condensation, dried under vacuum, and dissolved in acetic anhydride. This intermediate product is treated with one of the following: (1) 1 mole naphthalene sulfonated with 1–1.2 moles H_2SO_4 at 95°–100°C. and condensed with 0.5–0.25 moles HCHO added as the 35–40% solution and boiled for 10 hr.; (2) equal weights of 2-naphthol and H_2SO_4 heated for 4 hr. at 115°C., dissolved in water, and condensed with 0.25 moles HCHO at 95°–100°C. In either case the final product is partially neutralized with saturated Na_2SO_3 solution, followed by solid Na_2SO_3. Eventually the products are brought to pH 3.2–3.4 with acetic acid. These syntans are claimed to possess all the desirable properties of all types of syntans, including good molecular size resulting in full leathers, and rapid penetration. The product made with sulfonated 2-naphthol appears to be preferred because of the additional phenolic groups introduced and the low ratio of sulfonic to phenolic OH groups, but the product made with naphthalene sulfonic acid is cheaper. H.B.M.

Effects of the Kind of Tannin and the Concentration of Tanning Liquor on the Leather Properties. E. Sugano and K. Yamamoto. *Repts. Govt. Chem. Ind. Research Inst., Tokyo*, **53**, 242–49 (1958) (English summary).—Liquors from various tanning extracts containing 5 to 50% solids, adjusted to pH 4.4, were used to tan pieces of delimed steerhide for 30 days.

Water-soluble matter in the leathers decreased in this order: chestnut, soluble quebracho, Dulcotan, ordinary quebracho, Neochest, wattle. Water-soluble matter increased with liquor concentration. Vertical distribution of water solubles was very uniform for chestnut, Dulcotan, and Neochest. Fixed tannin decreased in this order: soluble quebracho, chestnut, wattle, ordinary quebracho, Dulcotan, Neochest. Fixed tannin was maximum from liquors containing 25–30% solids, decreasing at higher concentrations because of retarded penetration. Water absorption decreased in this order: ordinary quebracho, wattle, Neochest, chestnut, Dulcotan. Ordinary quebacho gave the darkest, and Neochest the lightest, color. Microstructure of the leather was little affected by kind of tanning extract. Tanning in liquors of 25–30% solids is recommended as giving the best microstructure, rapid penetration, good color, and low water absorption. Quebracho should not be used at concentration higher than 25%.

Authors' summary (abridged).

Chemical Studies on the Liming of Animal Skin. VIII. The Influence of Liming Treatment of Animal Skin on Formaldehyde Tanning and Chrome Tanning. H. Toyoda and A. Futami. *Repts. Govt. Chem. Ind. Research Inst., Tokyo*, **53**, 288–98 (1958) (English summary).—Effects of time of liming and of concentrations of sharpening agents on fixation of HCHO and T_s were studied with steerhide and goatskin. Fixation of HCHO increased with liming for tannage at pH 4, was unchanged for tannage at pH 6–8, and decreased for tannage at pH 11. At any pH value, T_s of HCHO-tanned skin decreased with time of liming. Both fixation of HCHO and T_s decreased with increasing concentration of dimethylamine and Na_2S in the lime liquor. Fixation of Cr from basic Cr sulfate increased with duration of liming, presumably because of increased number of available COOH groups resulting from deamidation. Time of liming had little effect on Cr fixation from Cr oxalate solution.

Authors' summary (abridged).

An Apparatus for Determining the Quality of Sole Leather by Fatigue Testing. J. Zilles. *Bor- és Cipo- technika*, **7**, No. 3, 70–71, (1957); *Hung. Tech. Abstr.*, **10**, 50 (1958).—To determine the intrinsic value of leathers they must be tested for the changes due to the consequences of the heavy and repeated physicomechanical and chemical stresses acting upon them. The changes observed upon the leathers can constitute a basis for determining the intrinsic value only of the factors causing them to act jointly and simultaneously. The apparatus reproduces the factors causing deterioration which act upon the sole leathers in the course of wear. The leather tested is bent back and forth continuously with a pressure conforming to the body weight acting upon it simultaneously. The specimens are tested in the above manner first in a dry state and then while immersed in water to determine the extent of elution. The effect of wear was not reproduced because the apparatus yields other data which are more reliable in respect to the actual resistance to wear than those obtained with conventional wearing apparatuses. Data expressible by indexes are obtained for the properties of the tissues (flexibility, elasticity, swelling, *etc.*); furthermore, data are obtained on the extent of elution which has a continuous influence on the actual resistance to wear. Changes in the resistance to flexure and in elasticity may be computed on the base of the automatically recorded curve, whereas the diverse properties of the leather can be calculated and numerically expressed by means of other data.

The Citrate Complexes of Iron(III) and Aluminum at Low pH. M. Bobtelsky and J. M. E. Goldschmidt. *Bull. Research Council Israel*, **7A**, 121–28 (1958); *Chem. Abstr.*, **52**, 16969*e*.

Alteration of Proteins and Amino Acids under the Influence of Ultrasonics. M. A. Khenokh and E. M. Lapinskaya. *Zhur. Obshchei Khim.*, **28**, 704–10 (1958); *Chem. Abstr.*, **52**, 17128*b*.

Effect of Temperature on the Rate of Cleavage of Procollagens by Collagenase. O. V. Kazakova, V. N. Orekhovich, and V. O. Shpikiter. *Doklady Akad. Nauk S. S. S. R.*, **120**, 359–60 (1958); *Chem. Abstr.*, **52**, 17339*d*.

The Interaction of Chromium Salts and Silicic Acid. M. S. Ovrutskii and M. A. Goronovskaya. *Legkaya Prom.*, **18**, No. 6, 43 (1958); *Chem. Abstr.*, **52**, 16968*c*.

The Chemical Nature of the Extractives from the Bark of Red Fir. E. S. Becker and E. F. Kurth. *Tappi*, **41**, 380–84 (1958); *Chem. Abstr.*, **52**, 17706*f*.

Brine Treatment of Sheepskins. I. Leontev. *Myasnaya Ind. S. S. S. R.*, **29**, No. 1, 17–19 (1958); *Chem. Abstr.*, **52**, 17769*a*.

Preservation of Hides in Brines of High Specific Gravity. A. Anfimov, V. Teites, and N. Smolskii. *Myasnaya Ind. S. S. S. R.*, **29**, No. 1, 15–17 (1958); *Chem. Abstr.*, **52**, 17769*b*.

Complex Ions of Chromium. VIII. Mechanism of Reaction of Organic Acid Anions with Chromium(III). R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis. *J. Am. Chem. Soc.*, **80**, 4469–71 (1958).—The rates of reaction between $[Cr(H_2O)_6]^{+++}$ and malonate, citrate, lactate, tartrate, glycolate, phthalate, acetate, and oxalate ions were studied by a polarographic method. The reactions were first-order with respect to Cr concentration. Rates of reaction were nearly independent of the kind of anion, increased with ionic strength in an approximately parallel manner for all the anions investigated, and were inversely proportional to pH value. Determination of the rate of reaction of citrate ion by a spectrographic method, which measures rate of formation of the complete chelate ring, gave the same reaction rate as the polarographic method, which is interpreted to mean that there is only one slow reaction in the whole sequence of reactions leading to formation of the Cr complexes. This slow step is believed to be the dissociation of an aquo group from the Cr complex. H.B.M.

War on the Cattle Grub — Past, Present, and Future. F. O'Flaherty. *Leather Mfr.*, **75**, No. 5, 5 (1958).—The history of the cattle grub, its life cycle, the effect it has on the animal and leather made from the hide of the

animal, the present attempt at its eradication, the economic aspects of its damage, and new attempts to be made at its eradication are mentioned and discussed. Graphs and photographs are used to show the grub, its life cycle, and damage done to animal and hide. J.J.

Leather Fungicides. Anon. *Leather Mfr.*, **75,** No. 7, 10 (1958).—The study by the National Bureau of Standards of hundreds of fungitoxic compounds for use on leather has indicated some of the factors necessary for a good fungicide, the deteriorating of some fungicides, deterioration effects of some fungicides on leather, and how substituents in some organic fungitoxic compounds increase or decrease their fungicidal effectiveness. Two substances, namely, bis (4-nitrophenyl) carbonate and bis (2-chloro-4-nitrophenyl) carbonate, show excellent results as fungicides on leather, but more work on these compounds is indicated before they can be adopted as official fungicides. J.J.

PATENTS

Tanning Mammalian Gut. Brit. Pat. 800,475. Ethicon, Inc. Appl. July 8, 1955.—The connective tissue layers of mammalian gut, mechanically treated to remove a major amount of fatty and non-collagenous proteinaceous material, are treated with a mild tanning agent, being such as to ensure no significant shrinkage of the tissue at temperatures up to 122° F., washed to remove said agent and steeped in an aqueous sodium salt of ethylene diamine polyacetic acid. Specified tanning agents are aqueous formaldehyde, sodium chloride, sodium sulphate, ammonium sulphate and potassium or ammonium aluminium sulphates. Tanning may take place in the presence of water for at least 24 hours, by immersion, e.g. in a saturated salt solution or by packing the wet gut in dry salt. In the examples, the steeping processes are identical with those disclosed in Specification 731,501, [*Group* IV (b)], to which reference is made, and thus involve a number of separate treatments with intermediate squeezing, and the use in the same liquor as the ethylene diamine polyacetic acid, of *n*-butanol; *p*-diisobutyl phenoxy polyethoxy ethanols and *p*-diisobutyl phenoxy polyethoxy ethylsulphate sodium salt or methyl dodecyl benzyl trimethyl ammonium chloride; ethylene glycol monoethyl ether; and ammonium hydroxide.

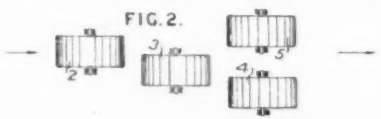
Stamping and Hardening Leather. Brit. Pat. 801,046. Schuhfabriken Odermatt & Co. A. G. Appl. Oct. 11, 1956.—Leather for shoe soles and heel-taps is treated in a stamping press, preferably after impregnation with a silicone resin which may be dissolved in a solvent such as benzol or toluol, the treatment in the stamping press being before the hardening commences, to produce depressions at least 1 mm. deep, rounded at the crest and at the bottom, and with inclined sides. The depressions may form grooves running mainly transverse to the longitudinal axis of the sole, circular grooves, or a net-like pattern, and in leather for adult use the grooves are preferably 2–3 mm. deep or more. The leather may be preheated before impregnation and brought into the press in the warm state and kept warm while there.

Stiffening Leather-like Agglutinated Fibre Materials. Brit. Pat. 801,483. Alegre, A. A. Appl. Dec. 16, 1954.—Porous artificial leather composed of natural or synthetic fibres bonded together with a latex of natural or synthetic rubber is hardened, i.e. stiffened, by placing it in a bath at not less than room temperature containing a hardening agent which does not react with the artificial leather but hardens it by penetrating into the pores of the fibrous structure of the artificial leather without destroying its porous characteristic, followed by drying, preferably at room temperature. The hardening agent may be casein, starch or starch derivatives, glues, gelatine, dextrin, carob seed, or natural or synthetic resins, e.g. vinyl resins with a plasticiser, and may be dissolved or dispersed in aqueous solutions which may contain wetting agents to assist in impregnating the artificial leather.

Waterproofing. Brit. Pat. 802,541. Farbenfabriken Bayer A. G. Appl. Aug. 1, 1956.—Textiles, leather and paper are rendered hydrophobic by treatment with a product formed by reacting an aliphatic primary monoamine containing at least 14 carbon atoms in the form of an organic salt with epichlorhydrin in the melt. The materials are impregnated with the product and subsequently heated for a short time. Advantageously an aqueous emulsion comprising, in addition to water, a minor proportion of the product and a major proportion of other hydrophobing agents, especially solid paraffins or waxes, and most advantageously together with a minor proportion of a zirconium or aluminium salt, is used. In examples a cotton fabric is impregnated with an aqueous solution of the reaction product obtained by melting epichlorhydrin with the acetic acid salt of octadecylamine and is subsequently squeezed off and dried at 125° to 135° C.; and a cotton cloth is impregnated with an emulsion prepared from solid paraffin, montan wax, water, the aforementioned reaction product and zirconium acetate and is subsequently squeezed off and dried at 120° to 130° C. Examples of other emulsions are also given.

Leather Rolling Machines. Brit. Pat. 801,543. Svit, Narodni Podnik. Appl. Sept. 27, 1955.—A leather-rolling machine having a series of work rollers

FIG. 2.



(2–5) with co-operating supporting rollers between which the leather is fed, is characterized in that the rollers are transversely staggered in respect of the direction in which the leather advances, preferably two or more work rollers (4, 5) being coaxial and spaced apart and a further two or more work rollers (2, 3) being non-coaxial and transversely staggered, so that the tracks of the work rollers over the leather overlap. Pairs of co-operating spring-loaded feed rollers (not shown) are provided in front of and behind each of the non-coaxial work rollers.

Skin-Softening and Dye-Fixing Composition. Brit. Pat. 800,827. General Aniline & Film Corporation. Appl. Nov. 9, 1955.—A detergent composition comprising an N-acyl taurine salt of the formula $R^2R^1N—CHR—CHR—SO_3M$. wherein R is H or a C_{1-3} alkyl radical, R^1 is H or a C_{1-20} hydrocarbon radical, R_2 is an acyl radical derived from an aliphatic or alicyclic carboxylic acid having at least 8 carbon atoms and M is an alkali metal (Na, K and Li specified) or alkaline earth metal (Ca, Mg and Ba specified), cation, together with an Na, K or triethanolamine salt of an aliphatic or alicyclic carboxylic acid having at least 8 carbon atoms may be used as an aid in softening hides and skins and as an aid in the fixing of dyes to leather.

Waterproofing Fabrics and Leather. Brit. Pat. 802,540. Midland Silicones, Ltd. Appl. Aug. 1, 1956.—In rendering fabrics, e.g. of glass, asbestos, paper, cotton, wool, rayon, "Orlon," "Dacron" (Registered Trade Marks), polyacrylonitrilevinyl chloride copolymers, linen, silk, cellulose triacetate and leather, water-repellent, a siloxane is deposited on the fabric by immersing it in a siloxane-in-water emulsion containing (1) a siloxane of the general formula $R_mSiO_{\frac{4-m}{2}}$ in which each R is a monovalent hydrocarbon or hydroxylated hydrocarbon radical or a hydrogen atom and *m* has an average value of from 1 to 3 inclusive, there being not more than one hydrogen atom in each unit; (2) a non-ionic emulsifying agent; and (3) from 0.2 to 80 per cent by weight of (1) of a polyimine of the general formula

$$Z(CH.CH_2.NH)_xCH.CH_2.Z,$$
(with R^1 substituents)

wherein Z is an NH_2 group or a haloyen atom, R^1 is hydrogen or a methyl radical and *x* has a value of at least 4, or a salt thereof or a polyglycol quaternary ammonium compound of the formula

$$HO\left[\begin{array}{l} NR''_3.Y \\ | \\ CH_2 \\ | \\ CH_2CHO \end{array}\right]nH$$

in which R^{11} is an aliphatic hydrocarbon radical of less than 5 C atoms, Y is an acide anion and *n* is at least 2 (*see* Group IV (a)), and thereafter removing the fabric and drying it. The emulsions may also contain urea and melamine aldehyde resins and preferably contain siloxane setting catalysts, e.g. triethanolamine titanate, diethanolamine titanite, triethanolamine titanate and sodium and zinc acetates. Examples are given.

Coated Fabrics and Paper. Brit.Pat. 801,475. Algemene Kunstzijdeunie N.V. Appl. Nov. 5, 1956.—Metals, fabrics, leather, wood, ceramic articles, films and foils are coated with solutions made by dissolving polyamides in an azeotropic mixture of water and 2-chloroethanol at a temperature of at least

80° C. The solutions may be buffered to a *p*H of 6.8 to 9.2 with borax and may also contain trichloroethanol, carboxy methyl cellulose, methyl cellulose, ethyl cellulose, plasticisers, dyes, pigments and solvents or non-solvents. In the examples: (I) and (II) paper is coated with a solution of poly-ε-caprolactam in an azeotropic mixture of water and 2-chloroethanol and dried; and (III) a boiling solution of ε-caprolactam in an azeotropic mixture of 2-chloroethanol and water is gelled, ground to a semi-liquid paste and coated on paper; the resultant coated paper being led over steam-heated rollers. Specification 544,715, [*Group* IV], and French Specification 874,720 are referred to.

BOOK REVIEW

An Introduction to the Chemistry of Fats and Fatty Acids. F. D. Gunstone. New York. John Wiley and Sons, Inc., 1958. 161 pp. $6.—The subject matter in this book is arranged to give a concise account of the aspects of the chemistry of fats and fatty acids. In general, courses in organic chemistry seem to bypass this particular field of study, and this book is set up to help fill this particular need.

The subjects covered in the various chapters are:

I—The Fatty Acids: Nomenclature; Classification; Saturated Fatty Acids; Unsaturated Fatty Acids; Branched-Chain Fatty Acids; Determination of Structure; Synthesis.

II—The Chemical Nature of Fats: Classification of Lipids; Methods of Determining the Chemical Constitution of Fats; The Component Acids of Fats; The Component Glycerides of Fats.

III—The Physical Properties of Fats: Melting Points; Polymorphism and Molecular Structure; Boiling Point; Monomolecular Films; Refractive Index and Molecular Refraction; Solubility; Spectra.

IV—The Chemical Properties of Fats and Fatty Acids: Hydrolysis and Esterification; Hydrogenation; Oxidation; Polymerization.

V—The Synthesis and Utilization of Fats in Living Organisms: Biosynthesis in Plants; Metabolism in Animals.

VI—The Chief Technical Application of Fats.

The portions pertaining to the chemistry of the fats and fatty acids are very complete. The chapter, however, on applications of the fats is very brief and merely a sketchy outline. In general it is a very good book for anyone contemplating doing work in the field of fats and oils, or for those desiring to know more of the complex chemistry involved.

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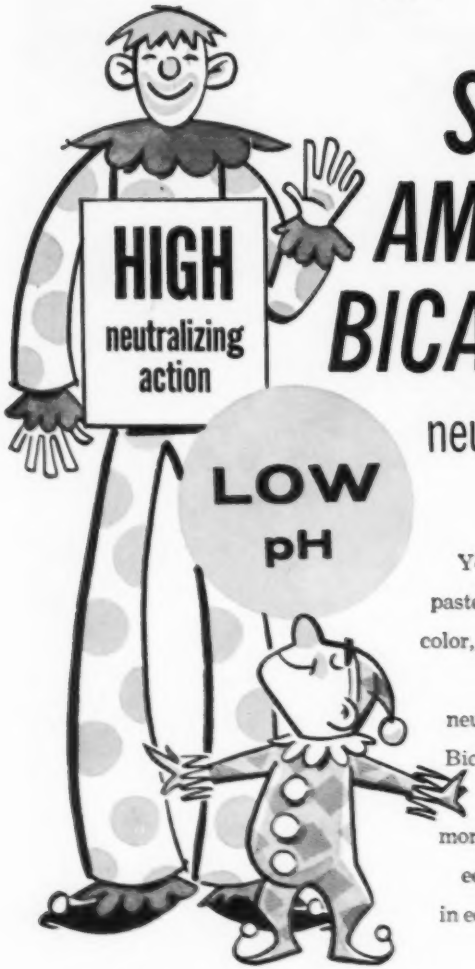

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New Esterified Oils Offer Major Benefits To White Tanners

An important development was announced recently by a leading manufacturer of tanning chemicals.

After considerable basic research, Seaboard Chemicals, Inc. is the first to offer the tanner a new concept in white leather fatliquors. It's a series of esterified oils called the Polarsols.

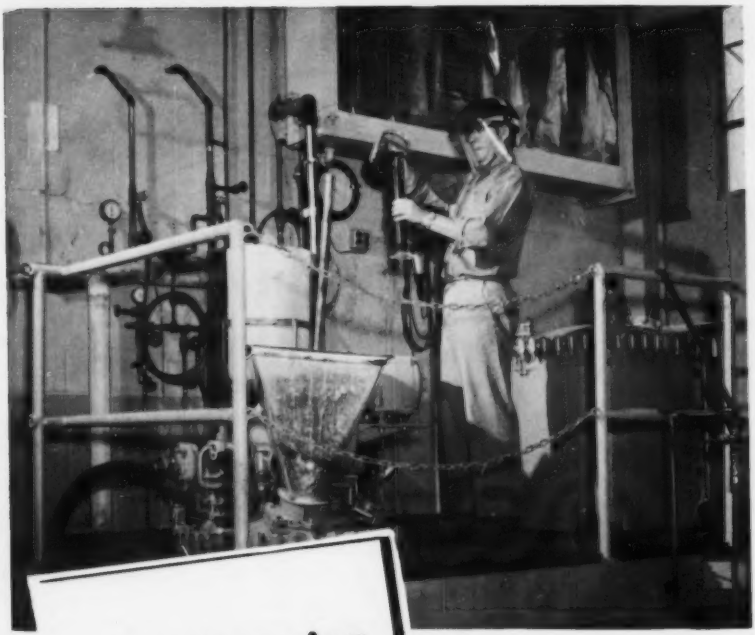
Tannery production runs indicate that these oils possess an attractive combination of properties that can help white tanners get more top-grade leather per pack and those already using the Polarsols claim the temper of their stock can be kept under absolute control, from mellow all the way to super-soft.

Unlike ordinary sulfated oils, which tend to produce looser leather as oil percentage increases, Seaboard's new esterified oils produce an overall tight break regardless of oil percentage used. Reports from the field indicate this is true even out into the flank and belly areas, with the result that an unexpected bonus of additional high-grade leather can be produced. And there is less trimming when the stock is finished.

To check oxidation characteristics, rigid Fadeometer tests have been conducted over a period of time on various types of leathers fatliquored with the Polarsols. These bleached esterified oils proved to be unusually light fast, easily passing 120-hour specifications. Also the Polarsols showed excellent stability where residual alum was present.

Perhaps one of the most attractive characteristics of these new esterified oils is the amount of money they save. According to Seaboard, the Polarsols soften leather to a greater degree than sulfated oils, so significant savings can be expected. Field experience has borne this out, with many tanners reporting they can get the same degree of softness in their stock with 20% less oil.

There is a Polarsol for every type of white leather—whether it be sides or splits, suedes or grains, kid or calf. The manufacturer offers percentage suggestions for use. To get detailed information and a trial sample of one of the Polarsols, specify your type of leather. Write or phone Seaboard Chemicals, Inc., Dept. 3G, 30 Foster St., Salem, Massachusetts, U. S. A. In Canada: Tennant Union, Ltd., Toronto and Montreal.



Manufacturing "Specs"...

This is the pilot plant in the laboratory where a new chemical can be produced in sufficient quantities for large scale tannery tests. When a demand is established the specifications will be ready for transfer of production to the plant.

CHEMTAN COMPANY
EXETER, NEW HAMPSHIRE

All our facilities are devoted exclusively to the tanning industry.